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Metal Particulate Emissions from Stationary Sources. Volume 1. Standard Sampling and Analysis Method

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A program was undertaken to develop reliable methods for measuring trace elements in emission streams. This program concerns a sampling and analysis method for arsenic, cadmium, chromium, colbalt, manganese, nickel, lead, selenium, and vanaduim. Based upon a review of the literature, atomic absorption spectrophotometry was selected as the analysis method for all metals. To approximate a stationary source, a simulation system consisting of a fuel oil combustion chamber and stack with sampling ports was constructed. Known amounts of metals were introduced to the system as organometallic additives to the fuel. Flue gas sampling was carried out simultaneously with two trains, permitting a direct comparison of changes in configuration, impinger solutions and sample recovery procedures. Based upon relicate experiments, precisions of 7 to 11 percent were obtained for all elements except As (15 percent) and Se (21 percent). Accuracies of Co, Ni, Mn, Cd, Cr and V were within 15 percent at the 100µg level, with Pb being 31 percent high and As and Se being low by 32 and 48 percent, respectively.

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Volume 1. Standard Sampling and Analysis Method

by

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ABSTRACT

Promulgated standards of performance for several new stationary sources include regulations for permissible levels of mass emissions. Many of these sources can contain trace levels of potentially hazardous metal species which, when present as particulate, are submicron. Such particulate can easily penetrate to the lower airways of the lungs, resulting in a hazard to health. As a result, a program was undertaken to develop reliable methods for measuring trace elements in emission streams. This report concerns a sampling and analysis method for As, Cd, Co, Cr. Mn, Ni, Pd, Se and V; a comparison report concerns the efficiency of collection filters for submicron hazardous metal particulate. Based upon a review of the literature, atomic absorption spectrophotometry was selected as the candidate analysis method for all metals.

To approximate a stationary source, a simulation system consisting of a fuel oil combustion chamber and stack with sampling ports was constructed. Known amounts of metals were introduced to the system as organometallic additives to the fuel. Flue gas sampling was carried out simultaneously with two trains, permitting a direct comparison of changes in configuration, impinger solutions and sample recovery procedures. After nitric acid digestion, samples were analysed by atomic absorption spectrophotometry. Based upon the results from preliminary evaluations, a Method 5-type train employing a quartz filter, 0.1 N HNO_3 impinger solutions, and special glassware precleaning and sample recovery procedures was selected for sample collection. Based upon nine replicate analyses, precisions of 7 to 11 percent were obtained for all elements except As (15 percent) and Se (21 percent). Accuracies of Co, Ni, Mn, Cd, Cr and V were within 15 percent at the 100 μg level, with Pb being 31 percent high and As and Se being low by 32 and 48 percent, respectively. In addition, an evaluation of Methods 104 and 101 for Be and Hg, respectively, gave good recoveries at the 1 g level. In the case of Hg, best accuracy was obtained when averaging at least 10 measurements of peak height. Recommendations are made for further work to consider the effect of eliminating 6 N HNO_3 from the sampling train cleanup procedure and to improve the recoveries of As and Se.

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SECTION 1

INTRODUCTION

Standards of performance for several new stationary source categories have been promulgated by the Environmental Protection Agency. Regulations for particulate emissions are generally related to permissible levels of mass emissions which are determined by sample collection and gravimetric analysis. Several recent technical publications have indicated that many of the potentially hazardous metal species present at trace levels in emission streams are largely submicron in particle size. Because of their size, collection by present control systems is not very efficient, leading to a potential for significant emissions to the atmosphere. Such submicron-sized particulate can be a hazard to health, penetrating to the lower airways of the lung when inspired. As a result, there is the need to develop reliable methods for measuring trace elements in emission streams.

Hazardous air pollutants are defined as those which "may cause or contribute to an increase in mortality or an increase in serious irreversible or incapacitating reversible illness". At present, asbestos, beryllium and mercury have been declared hazardous. Emission standards and sample collection and analysis methods have been promulgated for beryllium and mercury emissions from several source categories. Other trace metals, including lead, cadmium, vanadium, manganese, cobalt, nickel, arsenic and selenium have been implicated as possibly leading to health impairment. Before a standard can be set, it is necessary to develop suitable sampling and analysis procedures for that metal.

Additionally, the typical size of metal particulate for the elements of concern is reported to be in the range 0.1 - 1 μm, a size which corresponds to the poorest collection efficiency for stack sampling filters and for pollution control devices. Further information about the properties of high temperature particulate collection filters is therefore necessary to determine any limitations with respect to sampling and analysis methods.

To address these needs, an experimental program was developed and conducted in two concurrent phases. The results of this work are described in separate reports. Volume 1 describes the development of standard sample collection and analysis methods for nine metals and an evaluation of the promulgated test methods 101 and 104 for mercury and beryllium, respectively. Volume 2 presents a review of stack sampling filter requirements and provides characterization data for the most promising filter candidates.

SECTION 2

CONCLUSIONS

An evaluation of the collection and analysis of known levels of As, Cd, Co, Cr, Mn, Ni, Pb, Se and V (and, in some cases, Be) from stack emission samples leads to the following conclusions:

- A single stack emission sample can be analysed for all metals of interest. The procedure uses a Method 5-type sampling train with a quartz filter and 0.1 M nitric acid wet impingers. Special glassware precleaning and train cleanup procedures are required. After a nitric acid digestion of the combined samples from the collection train, analysis for each element is carried out by atomic absorption spectrophotometry.

- Based on nine replicate experiments at sample levels of about 100 µg for each metal, sampling and analysis yields a precision of 7 to 11 percent for all elements except As (15 percent) and Se (21 percent). The following accuracies (expressed as percentages) were obtained:

Pb	-	+31
Cd, Cr, V	-	+13 to 16
Mn	-	+6
Co, Ni	-	-2 to -4
As	-	-32
Se	-	-48

- The poor recoveries for As and Se may be due to incomplete combustion (oxidation) of the organometallic additives for these compounds, as the hydride evolution method is only suitable for the inorganic species of these elements.

- Analysis of Be at levels of 1 and 10 µg yielded good recoveries by Method 104 and by the sampling and analysis method described here for other metals.

- Evaluation of Method 101 for Hg yielded good recoveries at the 1 µg level. For best accuracy, the average of at least 10 measurements of peak height should be used for analysis.

SECTION 3

RECOMMENDATIONS

Further work is recommended with respect to simplifying the sampling train precleaning and sample recovery procedures and to improving the precision and accuracy for the analysis of As, Se and Pb.

Presently, the glassware is rinsed with concentrated HNO_3 during precleaning and sample recovery. It is recommended that the effectiveness of a 0.1 N HNO_3 rinse be evaluated. Besides reducing the risk of injury to operating personnel, this would reduce the number of samples to be collected. Furthermore, if shown to be suitable for sample recovery, the influence of 0.1 N HNO_3 on the stainless steel nozzle should be evaluated with a view to obviating the need to remove the probe liner for cleaning.

The low recoveries obtained for As and Se and the high recovery for Pb indicates problems with the sampling and analysis methods for these elements. Further studies should be conducted to identify the source of loss (or gain) for these elements. Specific areas to be considered include trace metal introduction into the combustion gas stream, losses within the combustion system, adequacy of the sampling train to collect these elements, recovery from the sampling train, sample workup procedure and analysis method.

SECTION 4

PROGRAM SCOPE AND EXPERIMENTAL APPROACH

SCOPE

The requested program to develop manual sampling methods for the measurement of emissions of hazardous air pollutants from stationary sources included the following specific elements:

a) Identify the analytical procedures for Pb, Cd, V, Mn, Co, Ni, Cr, As and Se which may be used in conjunction with manual sampling and identify those procedures which appear to be most suitable.

b) Design a stationary source sampling procedure for each of the above substances.

c) Test the promulgated EPA manual methods for beryllium and mercury and each of the recommended sampling and analysis procedures from (a) and (b) above in the laboratory.

d) Conduct field tests of the sampling procedures at five stationary sources which would be expected to be emitters of the tested metals.

e) Assess the accuracy, reproducibility, sensitivity and selectivity for each analytical method as well as the estimated combined error for the sampling train and analytical method for each hazardous substance.

At the onset of the study and as background for developing an experimental approach, sampling and analysis method features considered to be very desirable were identified as follows:

- As possible, utilize a common sample collection, pretreatment and analysis procedure for all metals.

- Based upon its general availability and application to source sampling, utilize a Method 5-type train for sample collection, with only those modifications to the train components or sampling protocol necessary to obtain suitable results.

- To simplify the train cleanup procedure, restrict sample recovery to the front half of the train (nozzle, probe and filter) for as many metals as possible.

- Attempt to achieve an accuracy and precision of 10 percent for combined sampling and analysis, assuming a metal concentration (in the stack gas stream) of 10 - 100 $\mu g/m^3$.

APPROACH

The development of a suitable sampling and analysis method for trace levels of the required metals depends upon an ability: 1) to collect an appropriate sample (without loss in the sampling train or contamination by sampling train components), 2) to quantitatively recover the sample, 3) to carry out suitable pretreatment steps for sample solubilization, concentration and avoidance of interferences, and 4) to carry out instrumental measurement of trace metals in the presence of large amounts of other matter with good precision and accuracy.

The experimental approach taken for this study included the following steps:

1. Based upon a review of the literature and our own background, select analytical methods for each of elements.

2. Construct an oil-fired source simulation unit providing stack conditions (principally, temperature and velocity) comparable to industrial sources. Known concentrations of metals are provided in the gas stream by organometallic additives to the fuel.

3. Prepare all-glass sample collection trains resembling those employed for Method 5 and including the back half impinger section.

4. Carry out simultaneous sampling runs with two trains for groups of metal additives. Simultaneous sampling permits the variation of one train parameter (filter temperature, impinger solution, etc.) to determine influence on sample recovery. Sample recovery and analysis is performed according to the developed protocols.

5. Continue evaluations, stressing multi-element additions and suitable sample workup and simplification in sampling, sample recovery and pretreatment protocols, as evaluated by sample recoveries.

6. For optimum procedure, carry out replicate evaluations with all elements to determine precision and accuracy for each metal.

7. Conduct field sampling tests to determine usability of the methods under field conditions.

SECTION 5

REVIEW OF ANALYTICAL METHODS

GENERAL

Specific analytical methods are required for eleven specified metallic elements present in emission streams at 10 to 100 $\mu g/m^3$. In selecting a method, several factors must be considered:

- Precision and accuracy for the concentration range of interest. Conventional particulate sampling involves a sample of 1-2 cubic meters. If separate sample aliquots are required for each element, detection limits of less than 1 μg may be required.

- Breadth of applicability. Obviously, the smaller the number of analytical techniques required, the smaller the investment in operator training, and possibly, the number of different sample preparation schemes required.

- Availability and state of development of the technique. In order for the sampling and analysis procedures developed in the program to be of maximum utility, the measurement techniques should be generally available in any well equipped analytical laboratory; they should not be unique to one or two locations across the country. Since the aim of this program is not to develop analytical methods, the ones chosen should be well characterized and in routine use.

- Simplicity and speed. The actual analysis time should be short. The amount of operator attention as well as operator expertise required should also be minimal.

- Sample preparation required. The complexity of the sample preparations required prior to analysis should be minimized. Similarly, wherever possible, the need for different sample preparations for different analyses should be eliminated.

There are currently available a number of instrumental analytical techniques, each of which is capable of detecting extremely minute quantities of a wide variety of elements. Techniques such as atomic absorption spectroscopy (AAS), flame emission spectroscopy (FES), X-ray fluorescence spectrometry (XRF), and neutron activation analyses (NAA) have been widely employed for performing elemental analyses such as the ones required in this program.

Several other instrumental techniques have potential applicability particularly for trace metals but they are not appropriate because they are not in routine use or because they are incapable of sufficiently precise measurements at the trace levels required. Atomic fluorescence spectrometry (AFS) is quite sensitive, but it is still a research technique; it is presently found primarily in university laboratories where custom made equipment is employed. Spark source mass spectrometry (SSMS) has high sensitivity and broad applicability; instruments are commercially available and in use in a fair number of laboratories, but sample preparation and accurate trace analyses with complex samples must still be considered a research project. Optical emission spectroscopy (OES) is widely used and is sufficiently sensitive, but it suffers from a lack of precision when measurements at trace levels are attempted.

Detection sensitivities obtainable with the four prime candidate techniques are presented in Table 1 for the elements of interest in this program. The listed valves are ideal condition detection limits, typically the amount of element required to produce a signal/noise ratio of 2. To make a measurement good to $\pm$ 10 percent, about 5 times more sample would be required. Presence of interfering species -- particularly for XRF and NAA -- can reduce usable sensitivity still further. The presence of one or more of a wide variety of chemical interferences, and/or imperfect optimization of instrument operating parameters can, and usually do, markedly decrease the sensitivity which is actually obtained. For practical purposes, the detection limits normally obtained routinely in most laboratories are probably 5-10 times higher than the levels presented in the table.

Table 1 shows that NAA is the most broadly applicable for the four techniques. It can detect all of the metallic elements of interest in this program. In terms of meeting sensitivity requirements, if one makes the reasonable assumption that the total sample volume can be reduced to 10 ml or less so that the entire sample can be radioactivated, the stated sensitivities should be adequate for all elements. In the presence of interfering elements, direct measurements could be considerably less sensitive. Most problems of interference can be surmounted; however, separation steps before or after activation and/or lengthly cooling periods between activation and counting are required to eliminate them. An important limitation is the relative unavailability of NAA facilities in comparison to other techniques.

X-ray fluorescence is more generally available than NAA, and with exception of the lightest elements (including beryllium) is generally applicable. The XRF is non-destructive and measurements of a number of elements can be made on a single sample. However, for many of the elements of primary concern in this work, it is less sensitive than atomic absorption.

TABLE 1

COMPARATIVE MAXIMUM SENSITIVITIES FOR
ATOMIC MEASUREMENT TECHNIQUES

	DETECTION LIMIT (μg)[a]			
ELEMENT	AAF (μg/ml)[b]	FE (μg/ml)[c]	XRF (μg/cm^2)[d]	NAA (μg)[e]
Be	0.002	NA	ND	15
V	0.02	0.01	0.007	0.002
Cr	0.005	0.005	0.019	0.3
Mn	0.002	0.005	0.014	0.0001
Co	0.005	0.05	0.003	0.01
Ni	0.005	0.03	0.010	0.7
As	0.1	50	0.010	0.005
Se	0.5	ND	0.012	0.01
Cd	0.005	2	0.002	0.005
Hg	0.2	40	0.090	0.08
Pb	0.03	0.2	0.030	0.5

NA - Sensitivity not available

ND - Analysis not normally performed

(a) - Under optimum conditions, presence of interferences or use of other than optimum instrumental operating parameters can produce significant individual or overall degradations (see text).

(b) - Atomic absorption with flame (Sources: J. D. Winedorfer and R. C. Elser, "Atomic Fluorescence Spectrometry," Anal. Chem. 43, 24A (1971); E. E. Pickett and S. R. Lpirtyoham, "Emission Flame Photometry - A New Look at an Old Method," Anal. Chem. 41, 29D (1969)).

(c) - Flame Emission (Source: same as b)

(d) - X-ray Fluorescence Multispectrometer for Rapid Elemental Analysis of Particulate Pollutants, EPA 600/2-76-033, J. Wagman, R.L. Bennett and K.T. Krepi.

(e) - Neutron Activation, weight of total sample can be in range of 0.01-10 g (Source: Anon., "Activation Analysis," Gulf General Atomic, San Diego, Calif.)

Of the remaining two techniques, atomic absorption and flame emission, the former is generally at least as sensitive, if not more sensitive, than the latter. Both are widely employed and instrumentation is present in most laboratories. FES is employed mainly for determinations of alkali and alkaline earth metals, while AAS is better developed for other metals which are of greater importance in this study. Atomic absorption is relatively interference-free, but the presence of high concentrations of dissolved salts can produce interference by scattering -- particularly in determinations performed at UV wavelengths. Atomic absorption is not as sensitive for certain of the important trace metals (arsenic, selenium, mercury) as it is for transition metals like chromium and manganese. However, modified AAS procedures can be employed to lower the detection limits listed in the table by a factor of 10 to 100. One such technique is the "flameless" measurement procedure for mercury. For arsenic and selenium, the metal ions in solution can be converted to AsH_3 and H_2Se which can be collected and introduced rapidly into the AAS flame. In addition to serving as a concentration step, the conversion to a gaseous species eliminates the presence of diverse salts which limit the AAS sensitivity for these three elements. With these modifications, AAS should have adequate sensitivity for all of the trace elements of interest in this study.

On the basis of the above, atomic absorption spectrometry (AAS) was selected as the preferred method for measuring the eleven trace elements of concern to this program.

LITERATURE REVIEW OF ATOMIC ABSORPTION SPECTROMETRY METHODS

A review of the recent literature on analysis of these elements at the trace level supports this choice of technique, both in terms of required sensitivity and in widespread usage of the technique.

A variety of new non-flame and modified-flame AAS techniques are being developed. Among these are the graphite tube furnace and carbon rod heater in the former category and the Delves cup and long-path tube burner in the latter. These techniques afford sensitivity increases from 2 to 200 fold over conventional AAS and hold the promise of less rigorous sample pretreatment. As yet they are not sufficiently well developed and standardized to warrant investigation for standard methods; however, this situation may change as they come into more common usage.

A survey of the literature was conducted in order to select the most appropriate conditions for AAS measurement of the eleven elements. As the object of this program was to obtain the most accurate, precise measure of these species, we have deliberately chosen to make measurements in concentration ranges where instrumental error and spectral interferences are minimized.

Table 2 lists appropriate concentration and mass ranges for accurate, precise measurement of the elements of interest; the mass ranges are calculated for a 10 ml final solution volume which is sufficient for analysis of only one or two elements.

A summary of the instrumental conditions generally used to obtain the most accurate measurement of these elements is given in Table 3, together with a notation of possible interferences that might be present in a stationary source environment. A more detailed discussion of points pertinent to each element is given in the text.

Arsenic

The most sensitive wavelengths for arsenic lie in the far UV at 194 mm and 197 mm. At these wavelengths the background absorption due both to aspirated salts and to the flame itself severely limits the sensitivity. While use of an argon/hydrogen/entrained air flame gives a lower background than acetylene/air for direct aspiration of sample into the flame, the presence of aspirated solids is still a problem. In this mode, the method has a usual concentration range of 1-50μg/ml.

The generation of arsine using various reducing agents and direct introduction of this gas into the flame has been reported by a number of authors who used zinc and stannous chloride[1], magnesium plus titanium trichloride[2] and sodium borohydride[3]. The sodium borohydride procedure of Fernandez[3] appears to be the easiest to use. In this arsine generation procedure, the acidified sample is transferred into a closed vessel that is connected via a stopcock valve to the argon inlet on the AA burner head. The vessel is purged with argon and then the solid reducing agent (sodium borohydride, for example) is added to the solution. The evolved gases (hydrogen plus arsine) are collected for a suitable length of time in the closed system, which is equipped with an expandable reservoir on a side arm, and are then purged into the flame by diverting the argon flow through the vessel. The passage of the arsine through the burner produces a peak or spike on the instrument output signal, the height of which is proportional to the mass of arsenic in the aliquot of sample taken for analysis.

By eliminating the solution (and salts) flow through the flame, the background is decreased markedly resulting in the much lower measurement range listed in Table 2.

An alternative method for measuring low levels of arsenic in the event that the AAS method had not worked well was the well-established silver dimethyldithiocarbamate colorimetric method, which has a range of from 1μg to 15μg of arsenic (in 10 ml solution) for accurate measurement.

Beryllium - The present Environmental Protection Agency (EPA) reference method for beryllium recommends AAS measurement in hydrochloric acid solution in a nitrous oxide/acetylene flame following wet ashing with

TABLE 2

CONCENTRATION RANGES FOR ACCURATE MEASUREMENT BY AAS

ELEMENT	CONCENTRATION RANGE IN SOLUTION	MASS RANGE FOR ACCURATE MEASUREMENT (Assuming a 10 ml volume of solution)
Arsenic	0.02 - 2µg[(a)]	0.02 - 2µg[(a)]
Beryllium	0.03 - 3µg/ml	0.3 - 30µg
Cadmium	0.02 - 2µg/ml	0.2 - 20µg
Chromium	0.1 - 5µg/ml	1 - 50µg
Cobalt	0.2 - 5µg/ml	2 - 50µg
Lead	0.5 - 20µg/ml	5 - 200µ
Manganese	0.05 - 3µg/ml	0.5 - 30µg
Mercury	0.01 - 0.5µg[(c)]	0.01 - 0.5µg[(c)]
Nickel	0.2 - 5µg/ml	2 - 50µg
Selenium	0.02 - 2µg[(b)]	0.02 - 2µg[(b)]
Vanadium	2 - 150µg/ml	20 - 1500µg

(a) Arsenic via AAS with generation of AsH_3 - entire sample used

(b) Selenium via AAS with generation of SeH_2 - entire sample used

(c) Mercury via "flameless" AA procedure - entire sample used

TABLE 3

AAS INSTRUMENT CONDITIONS FOR ACCURATE MEASUREMENT

ELEMENT	MEASUREMENT WAVELENGTH (nm)	FLAME*	INTERFERENCES
Arsenic	193.7	Ar/H_2	
Beryllium	234.9	N_2O/acet. - reducing	Al, Si, Mg may interfere - add 8 hydroxyquinoline
Cadmium	228.8	air/acet.	
Chromium	357.9	air/acet. - reducing	Fe, Ni may suppress, add NH_4Cl
Cobalt	240.7	air/acet.	
Lead	283.3	air/acet.	
Manganese	279.5	air/acet.	
Mercury	253.7	"cool vapor"	
Nickel	232.0	air/acet.	
Selenium	196.0	Ar/H_2	
Vanadium	318.3	N_2O/acet. - reducing	Al, Ti enhance, add excess Al

*acet. = acetylene

nitric, sulfuric and perchloric acids[4]. Aluminum, silicon and other elements may interfere but they can be controlled by addition of 8-hydroxyquinoline (for aluminum and silicon and large amounts (10% w/v) of potassium chloride (for alkali metals) .

Cadmium - Can be measured using an air acetylene flame in acid solutions which result from treatment and workup of various sampling train components. This procedure has also been recommended by Stanford Research Institute[6]. In the event of some unforeseen matrix problem, cadmium can be extracted into ammonium pyrollidine dithiocarbamate in methyl isobutyl ketone (APCD/MIBK) or as cadmium iodide (from 0.1 M potassium iodide) into MIBK.

Chromium - Chromium can be measured directly in acid extracts using a fuel rich air/acetylene flame; however, there are many suppressive interferences, including virtually all of the transition metals. It has been reported that the addition of sodium sulfate (10 mg per ml) will effectively eliminate all interferences[7].

Alternatively, chromium can be extracted into MIBK from 3 M hydrochloric acid.

Cobalt - Cobalt can be measured in air/acetylene flame. No interferences have been reported. Cobalt may be extracted into APDC/MIBK if necessary[8].

Lead - Lead can be measured directly by aspirating the acid solution into an air/acetylene flame. Various reports are at odds regarding the interference of anions such as sulfate and phosphate, as well as cations such as aluminum. Trace levels of lead can be concentration, and simultaneous elimination of possible interferences can be accomplished by extracting lead with APDC/MIBK after adjusting the solution pH to approximately 2.5 to 3 (Ref. 8, pp. 411-412).

The SRI method[6] recommends low temperature (plasma) oxidation to remove trace organics which are claimed to interfere in the direct measurement of lead. The wet oxidation pretreatment is expected to eliminate this problem.

Manganese - The direct measurement of manganese in an air/acetylene flame affords a sensitive measure of the manganese content of acid solutions. Very few interferences have been reported in the flame.

Mercury - The so-called "flameless" AAS technique in which ionic mercury is reduced to elemental mercury, and the mercury vapor then sparged into an optical cell mounted in place of the flame in the AAS spectrometer has been shown by many authors to be a reliable technique for the measurement of trace amounts of mercury. The mechanics and the chemistry vary somewhat from one investigator to another.

In general, the reduction of the ionic mercury (usually deliberately pre-oxidized to mercury (II) is accomplished in an acid by addition of a hydroxylamine salt and a stannous salt. The former is added first to remove any excess oxidants (nitrogen oxides, etc.) before reduction of the mercuric ion with the stannous compound. The recently published EPA reference method for mercury in stationary source emissions (Ref. 4, pp. 8835-8845) and the SRI report[6] recommend reduction in alkaline solutions with hydroxylamine only. The present literature survey and past knowledge has not uncovered a report of investigation of this procedure in the open literature, a finding corroborated by one of the authors of the SRI report[9]. The method may have merit in regard to minimizing the reagent blank in that no stannous reagent is required.

Nickel - The direct measurement of nickel can be made in an air/acetylene flame. No significant interferences have been noted (Ref. 8, p. 321).

Selenium - Like arsenic, the principal spectral lines for selenium lie in the far UV, and hence direct aspiration of solutions into the flame will lead to high background signals and poor sensitivity. The hydride evolution methods applied to arsenic have also been used successfully for selenium[1,2,3].

In the event that the hydride evolution - AAS method did not work out, an alternative method for measuring selenium was the well-established colorimetric method in which the selenium reacts with diaminonaphthalene to yield the colored piazselenol . This method has a range of 5-200 µg of selenium using 10 ml of sample and 50 ml of toluene to extract the colored species. The lower limit can be extended by changing the volume of toluene.

Vanadium - Vanadium is best measured by direct aspiration into a reducing nitrous oxide/acetylene flame. Both aluminum and titanium have been reported to enhance the vanadium absorption (Ref. 8, p. 280-1).

SAMPLE TREATMENT PRIOR TO MEASUREMENT

The choice of atomic absorption spectrometry as the preferred measurement method requires that all of the species of interest be dissolved prior to measurement. As the elements of concern in this program are metals or metalloids, the use of an acid solvent for initial extraction and solubilization of most of the materials, and a subsequent fusion of any insoluble material with an alkali carbonate is appropriate.

A mixture of nitric and hydrochloric acids would be best for dissolution of all metallic species. However, the presence of chloride during evaporation of the excess acid is likely to result in significant losses of elements which form volatile halides such as arsenic, selenium and vanadium.

The recent Stanford Research Institute report on manual methods for various metals in stationary source emissions recommends use of 8N nitric acid for impinger solutions, filter extraction and sampling train cleanup[6]; however, no basis is given for choice of acid and concentration. Sulfuric acid is not used because of the formation of insoluble lead sulfate.

The addition of perchloric acid was not deemed necessary as we planned to use and recommend only glass-fiber filters, and hence did not anticipate large amounts of organic matter.

A major goal of this program was to establish, if possible, a single procedure for sampling and sample pretreatment which would be adequate for all (or nearly all) of the elements of concern, although it was recognized that such pretreatment might not be the optimum (in terms of time and reagents) for each individual element.

In view of the decision to use quartz-fiber filter media, the alkali carbonate fusion originally proposed as a method for handling possible acid-insoluble residues was rendered impractical on a number of counts. The amount of alkali required would be greatly increased to dissolve the filter, giving an extremely high alkali background for atomic absorption measurement, and in addition adding to the solution a large amount of silicate that is known to interfere in the measurement of lead. This problem could be avoided by substituting treatment with hydrofluoric acid to eliminate the silica as the (volatile) fluoride. Another potentially more serious problem lies in the fact that while the glass fiber surface may have relatively low amounts of elements which are acid-extractable, the fiber matrix is likely to contain substantially larger amounts of these elements. Thus, complete dissolution of the filters may result in substantially higher background or "blank" levels. It was decided that complete dissolution of the filter would be pursued only if the recovery of elements from samples representing source tests was low.

SECTION 6

EXPERIMENTAL APPARATUS AND METHODS

SIMULATED SOURCE APPARATUS

In order to carry out sampling experiments under conditions representative of field sources, a simulated source apparatus was designed and constructed for use in the evaluation of sampling and analytical methods for the hazardous metals. In practice, trace metal particulate in a gas stream was generated through the combustion of fuel oil containing known amounts of organometallic additives. Measurement of the volume of gas passing through the simulated source apparatus during combustion of the metal-containing fuel, together with the quantity of fuel burned, permitted calculation of the concentration of the metals in the combustion gas stream. The collection and analysis of metals in stack gas samples and comparison to the added concentrations permitted an evaluation of sampling and analysis procedures.

Engineering Basis

Several factors were considered in planning the design of the equipment, as follows:

- Source Characteristics

Temperature range	120-230°C	(250-450°F)
Velocity range	900-3000 cm/sec	(30-100 ft/sec)
Moisture content	10-20%	
Particle loading	0.6-3.0 mg/m^3	(0.01-0.05 gr/SCF)

- Other Considerations:

  Duct size and length
  - Influence on gas flow
  - Influence on sample collection

  Particle Losses
  - Collection in duct
  - Exit gas cleaning
  - Other

  Fuel
  Dilution air requirements
  Sampling Rate
  Concentration of metal additives

- Design Summary

Fuel consumption:	1 ml/sec	(1 gal/hr)
Duct:	20 cm diameter	(8" diameter)
Stack gas temperature:	150°C	(300°F)
Stack gas volume:	8850 m/sec	(29,500 ft/sec)
Trace metal loading:	~100$\mu g/m^3$	

Further design considerations are presented in Appendix A.

Apparatus

A schematic drawing of the simulated source apparatus is given in Figure 1. The apparatus consists of a home oil burner system, a combustion chamber, flue duct work (including sampling ports) and an exhaust fan.

The burner system was purchased as a package and includes a fuel pump, electric ignition system, combustion air blower, and a fuel atomization and combustion tube. Fuel is delivered at a constant rate of 0.75 gallons per hour to the atomizer (hydraulic type). As is shown in Figure 1, the burner system is bolted onto a metal table-like structure oriented so that the flame is directed vertically. The atomization combustion tube projects through the table top with the pump, blower, and ignitor located below the table. There are two separate oil reservoirs (glass carboys). A valving arrangement permits rapid switching of oil flow from one reservoir to the other. In operation, one reservoir contains oil spiked with organometallic additives and the other, "pure" oil. At the beginning of a run, pure oil is burned. Simultaneously with the initiation of sampling, the reservoirs are switched by activating the appropriate valves so that spiked oil is burned. At the completion of the sampling period, the reservoirs are again switched.

The quantity of fuel spiked with organometallics that is burned may be obtained from the difference in weights of the spiked oil reservoir measured before and after the experiment.

The simulation source combustion chamber consists of three concentric stainless steel cylinders surrounding the atomization-combustion tube. Each cylinder is supported on hangers with small cross-sectional areas so that it floats thermally. Dilution air which has been passed through an absolute filter (HEPA) enters through ports in the housing surrounding the combustion chamber. The size of the ports may be varied with a sleeve type arrangement to control the quantity of dilution air. Mixing of dilution air and hot gases from the flame occurs just above the combustion chamber.

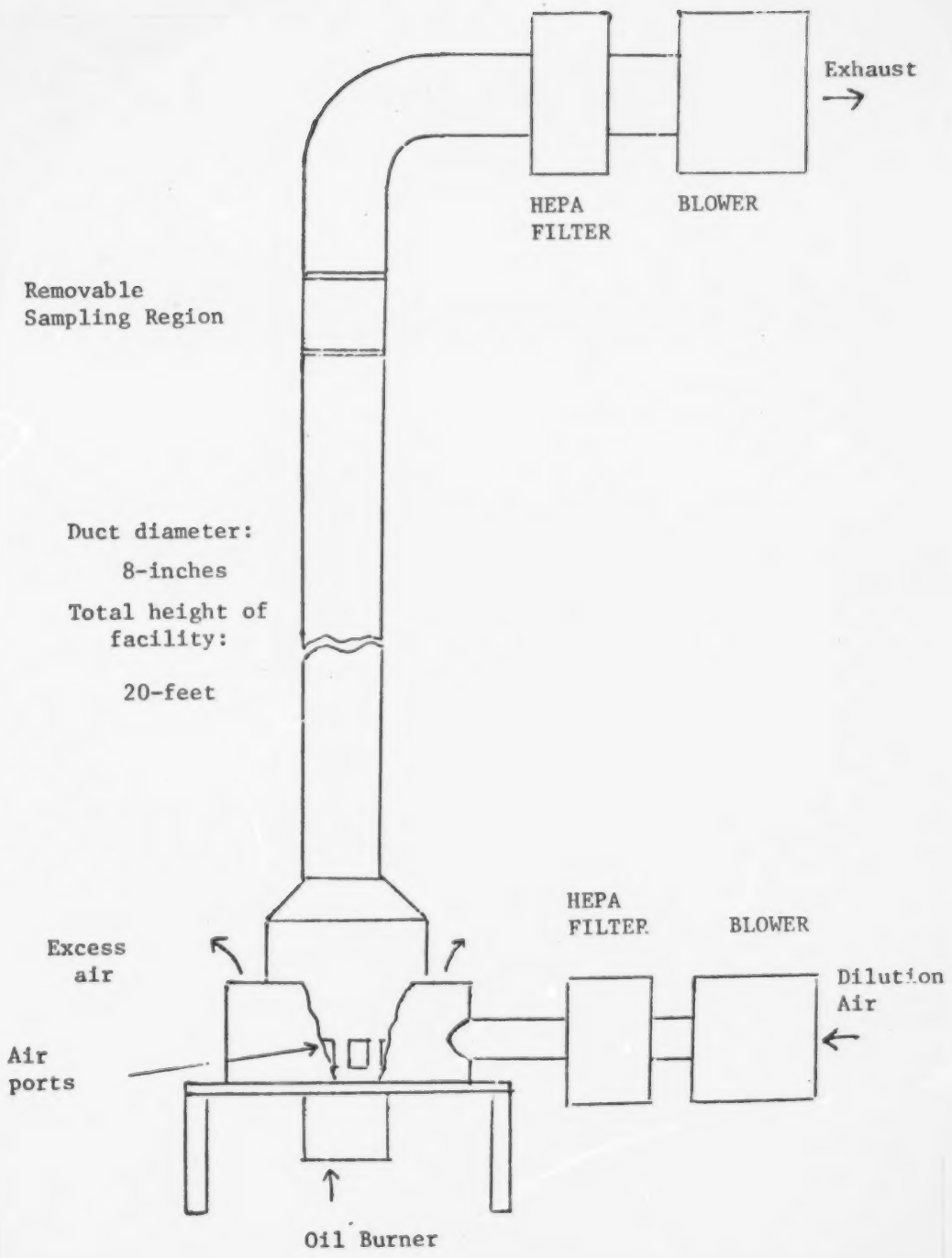

Figure 1. Schematic drawing of simulated source apparatus.

Diluted combustion gases pass up the flue shown in Figure 1 to the sampling region which is about 10 feet above the combustion chamber. The flue duct work is eight inches in diameter and is constructed of stainless steel. The flue section between the combustion chamber and the sampling section is insulated with fiberglass to minimize heat loss.

The sampling section of the flue duct work has two three-inch ports for inserting sample extraction probes. Above the sampling ports, there are also special ports for inserting temperature and velocity measuring. These ports were arranged 120°apart around the circumference of the duct so that complete traversals could be made along two perpendicular diameters. Temperatures were measured with an unshielded iron-constantan thermocouple and gas velocities with a standard pitot tube.

Downstream of the sampling section the combustion gases pass through an exhaust blower and then to the outside. A damper was placed in the duct downstream of the exhaust blower for controlling the gas flow rate through the system.

To provide isolation from the pilot plant environment, and the possibility of trace metal contamination therefrom, separate housings were constructed around the combustion and sampling sections of the apparatus, as shown in Figure 2. Filtered air was supplied to these housings to maintain them at positive pressure.

Experimental parameters that can be varied include the flue gas velocity and temperature and the trace metal additives and concentration. Gas velocity through the flue duct is controlled by the exhaust fan damper and to a lesser extent by the dilution air port size. The temperature of the flue gas is controlled by the ratio of dilution air to combustion air. Temperature and ve-ocity are consequently not independently controllable. Typical operating conditions are:

- Temperature - 150-160°C (300-320°F)
- Velocity - 9-11 m/sec (30-36 ft/sec)
- Total Gas Flowrate - 16-20 m^3/min (600-700 cfm)
- H_2O Content (determined by water collection in sampling train) - 1-2%

SAMPLING APPARATUS

As a result of their widespread application and availability, the evaluation sampling trains closely resembled Method 5 type trains for particulate sampling. The trains consisted of a nozzle and probe, filter, impinger section, gas meter and pump. During most of the evaluation runs, an all-glass system was used to avoid possible contamination from metal surfaces. One end of the 122 cm (48 inch) long by 1.6 cm (0.63 inch) diameter probe

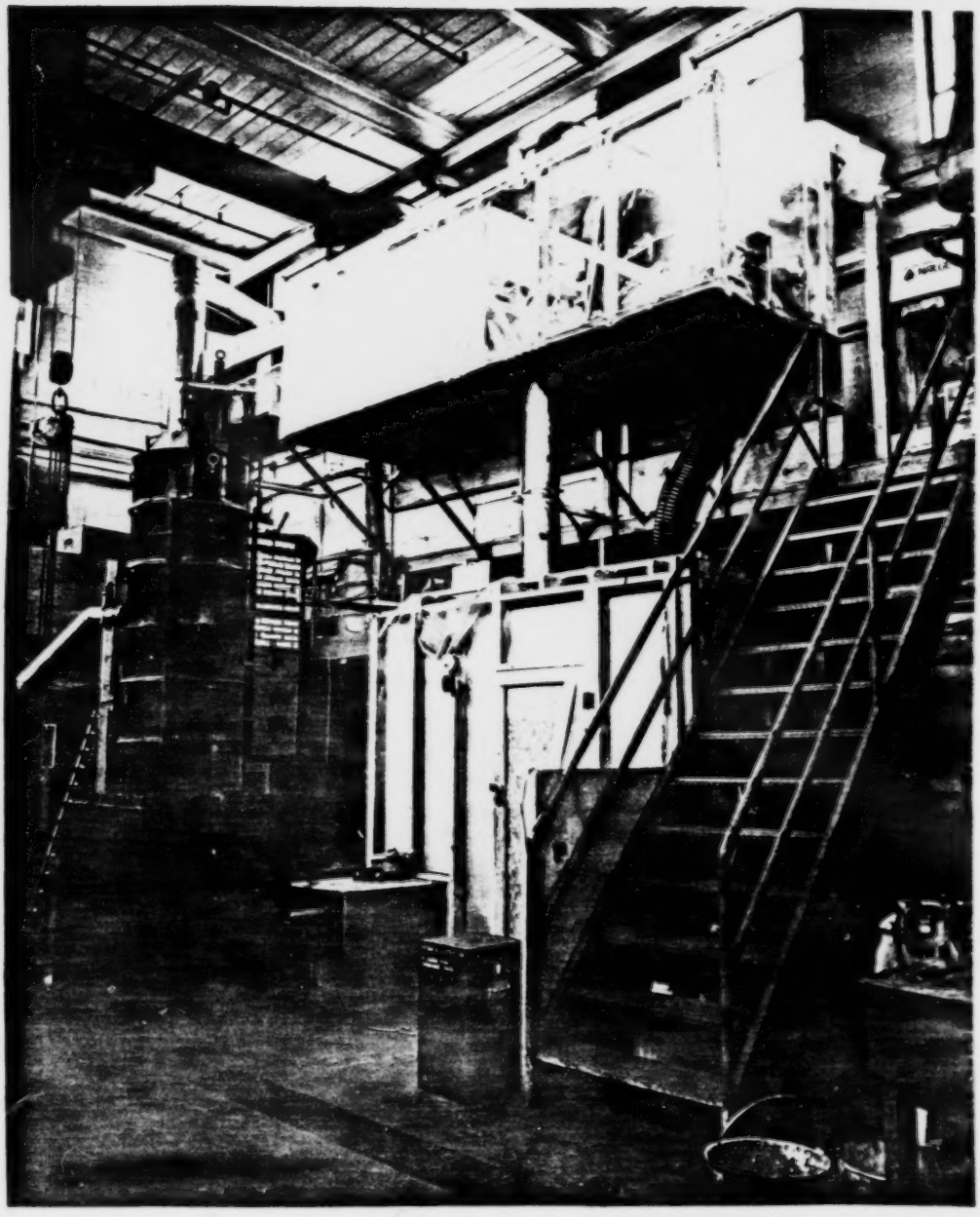

Figure 2. Photograph of simulated source apparatus.

was formed into a standard buttonhook nozzle with a 6.4 cm (0.25 inch) diameter opening. The probes were not heated during sampling since the moisture content of the flue gas is low (< 2 percent) and no condensation occurs.

The trains utilized 10 cm (4 inch) diameter filters maintained at 120°C (250°F). Because of their high purity, either strengthened tissue quartz (commercial) or ADL/Balston Microquartz (research) filter media were employed. The first and second impingers were of the Greenberg-Smith design, containing 100 ml of the selected scrubbing solution (either water, 6N or 0.1 N HNO_3), the third was left empty as a knockout trap and the fourth impinger contained about 200 g (preweighed) of silica gel.

Prior to each evaluation run, the glassware (impingers, filter holder, probe, etc.) was soaked overnight in an alconox-water solution, washed with the same solution (with brushing), rinsed with hot water, acetone and finally with 8N HNO_3. The glassware was given a final rinse with distilled water just prior to train assembly.

For sampling, the probes were inserted into the sampling ports in the burner flue and the filter holders preheated to about 120°C. Weighed quantities of the selected metal additives were premixed with a small volume (50-100 mℓ) of the fuel. This mixture was then added to the reservoir which was previously filled with an appropriate quantity of fuel. The burner system was started and allowed to run for one half hour to bring the system to equilibrium operating conditions. Velocity and temperature profiles across the flue duct were taken for calculation of the total gas flowrate through the duct and for setting of isokinetic sampling conditions. The fuel reservoirs were then switched and sampling initiated. A sample volume of about 1.75 cubic meters was taken under isokinetic sampling conditions. At the end of the sampling period, sampling pumps were shut off and the fuel reservoirs immediately switched. The spiked fuel reservoir was then weighed to obtain the weight of spiked fuel consumed. A sample of the spiked fuel was also taken after completion of each sampling experiment for metals analysis.

Upon completion of a run, the train was immediately disassembled and samples recovered. The filter was stored in a plastic petri dish. Catches from the impingers were combined (for specific cases, the contents of the first impinger were separated from the combined contents of the second and third impingers) and the total liquid volume was measured and stored in a previously cleaned polyethylene bottle. The impingers were then washed with 0.1N and 6N HNO_3 and the rinses were added to the impinger catch.

The probe was cleaned with water and acetone, using a clean buret brush to remove any visible particulate matter. The probe was then washed with 0.1N and 6N HNO_3. All probe washes were stored in cleaned polyethylene bottles. The silica gel was recovered and weighed to obtain the water content of the sampled streams.

In summary, the following samples were taken from each train:

1. filter
2. combined impinger catches*
3. acetone probe wash
4. nitric acid probe washes

A sample of the HNO_3 was reserved for determination of metal blanks. After sample recovery, glassware was placed in an alconox-water solution for overnight soaking.

METAL ADDITIVES

The trace hazardous metals of concern fall into categories of very low volatility (V, Co, Ni, Cr, Be, Mn), moderate volatility (Pb, Cd, As, Se) and highly volatile (Hg). Except for Hg, the oxides are quite stable at 150°C. The oxides of As and Se, however, have high vapor pressures at 150°C and attention must be given to their evaporative loss rate from filters. As a result, the metals of concern fall within four categories, as follows:

V, Co, Ni, Cr, Be, Mn	- low volatility, stable oxides
Pb, Cd	- moderate volatility, stable oxides
As, Se	- moderate volatility, volatile oxides
Hg	- high volatility, unstable oxide

As a result, experiments were planned in which at least one species from each category is included to properly evaluate the broadest range of emission forms.

Any of the distillate fuels are known to be quite free of trace hazardous metals. For this program, 250 gallons of No. 2 home heating oil was purchased from a local supplier and stored in clean 55 gallon drums. Prior to use, the fuel was filtered to remove any oxidation products or other particulate contaminants. Analysis of the fuel for several trace elements, expected to be present in the highest concentrations, revealed levels far lower than contemplated for the organometallic additions. Atomic absorption measurements of the fuel yielded Mn = 0.07 ppm, Ni = 0.04 ppm and V = < 0.05 ppm.

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*In some cases, the contents and wash of the first impinger was kept separate from those of the combined second and third impingers.

Based upon their solubility and availability, the following organometallic compounds were utilized for metal additions to the fuel:

beryllium acetylacetonate
vanadyl napthenate
mercury napthenate
nickel octanoate
cadmium octanoate
manganese octanoate
chromium octanoate
lead octanoate
cobalt octanoate
triphenylarsine
diphenyl selenide

The first series of experiments with a metal additive were planned with Mn which yields a stable oxide and is not present anywhere in the system as a potential contaminant, thus permitting an analysis of system memory and sample recovery.

SAMPLE PRETREATMENT PROCEDURE

As discussed in Section V.C, aqueous nitric acid is the preferred solvent for dissolving all of the elements of interest. The manual methods recommended by SRI employ 8 N nitric acid, which is presumably a 1:1 mixture of 70% nitric acid (the usual laboratory reagent) and distilled water. Based upon past applications experience in this laboratory, 6 N nitric acid was employed for the strong acid concentration.

Separate tests of the dissolution behavior of the various compounds in nitric acid were not carried out. The literature suggests that all of the metal carbonates, most of the oxides and the elements themselves are soluble in nitric acid, particularly when it is hot.

For the first series of evaluation runs (through Run 19), acid extracts from the individual sampling train components and solutions were analyzed separately in order to ascertain the distribution of these elements throughout the train. The sample treatment procedure employed for the analysis of individual components is shown in Figure 3.

For later runs, the solutions and extracts were combined, after some treatment, and measured as a single solution. A schematic presentation of this procedure is shown in Figure 4.

MEASUREMENT METHODS UTILIZED

Atomic absorption spectrophotometry was the method of choice for measurement of the elements of interest. Direct measurement without prior extraction was used for all elements. The instrumental conditions are

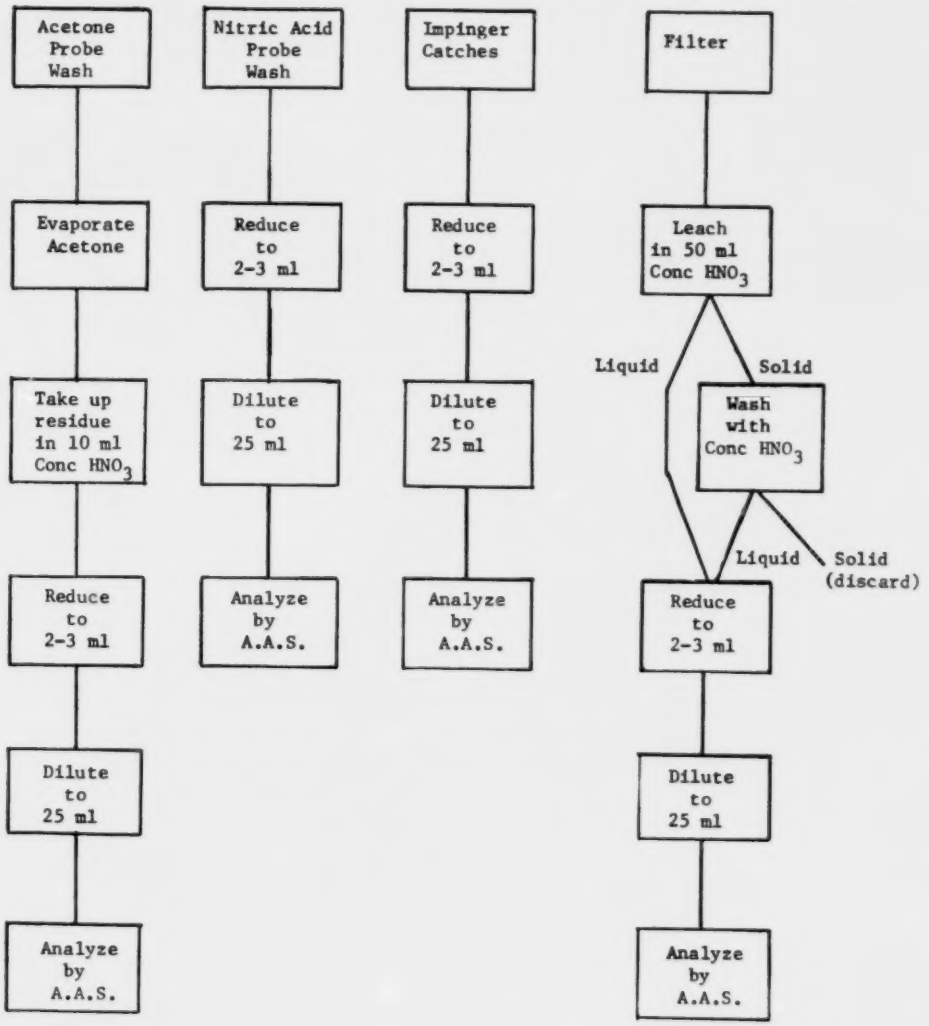

Figure 3. Sample treatment - separate train components.

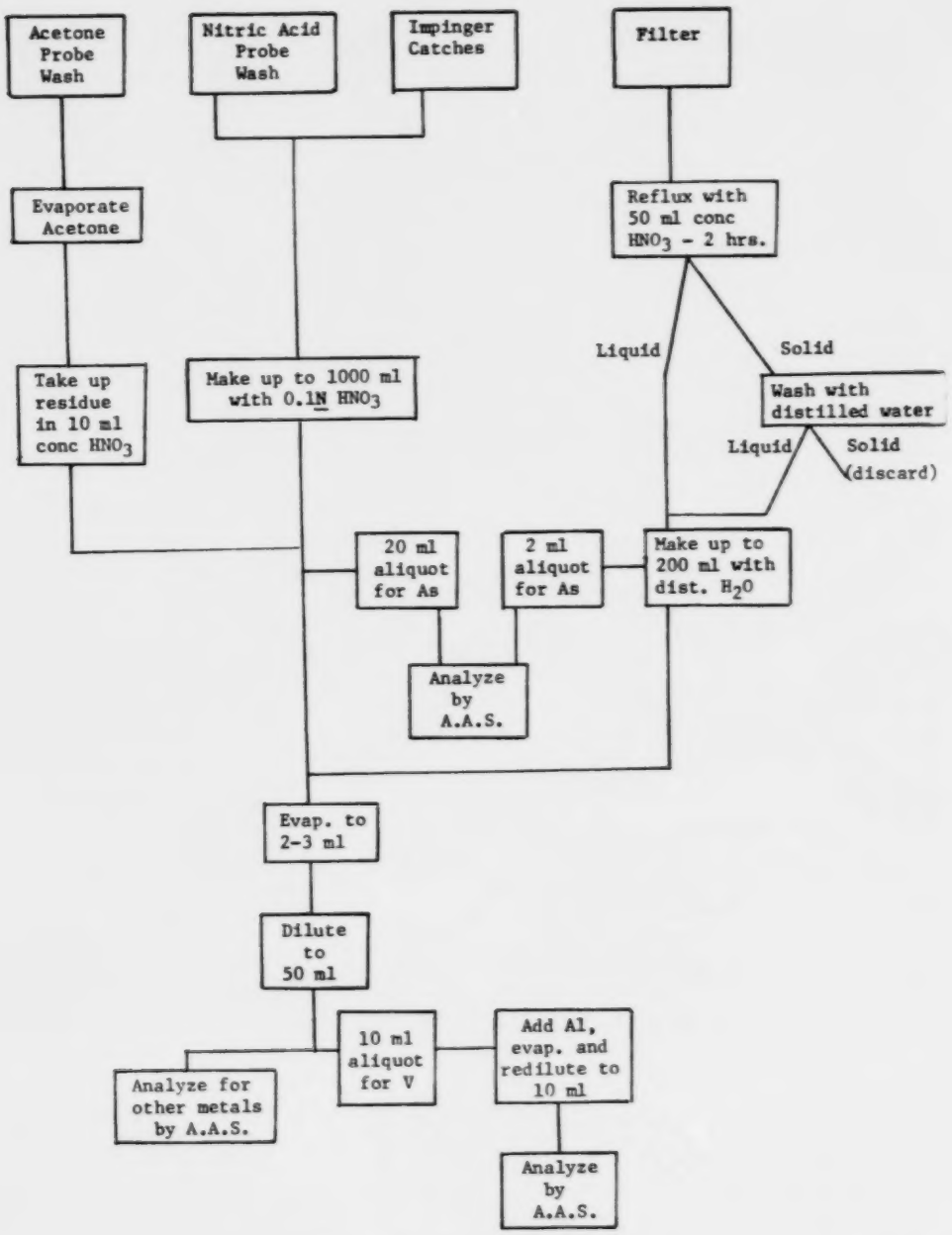
Acetone Probe Wash
Nitric Acid Probe Wash
Impinger Catches
Filter
Evaporate Acetone
Reflux with 50 ml conc HNO_3 - 2 hrs.
Liquid
Solid
Take up residue in 10 ml conc HNO_3
Make up to 1000 ml with 0.1N HNO_3
Wash with distilled water
Liquid
Solid (discard)
20 ml aliquot for As
2 ml aliquot for As
Make up to 200 ml with dist. H_2O
Analyze by A.A.S.
Evap. to 2-3 ml
Dilute to 50 ml
10 ml aliquot for V
Add Al, evap. and redilute to 10 ml
Analyze for other metals by A.A.S.
Analyze by A.A.S.

Figure 4. Sample treatment - combined solutions and washes from train.

summarized in Table 3; as is usual, the instrumental conditions were optimized while aspirating a standard solution of the particular element.

For measurement of vanadium, the measured solution was doped with 1000 mg/l of aluminum (added as the nitrate salt) in order to overcome any variable enhancement resulting from the presence of small, varying amounts of aluminum and/or titanium in the samples.

All atomic absorption measurements were made on a Perkin-Elmer Model 503 atomic absorption spectrophotometer equipped with a Hewlett-Packard Model 7100B chart recorder.

METAL CONTENT OF SPIKED OILS

The procedure for measuring the metal content present in the spiked oils involved extraction of the metals with aqueous acid and subsequent measurement of the metals in the extracts using atomic absorption spectrophotometry. For measurement of elements other than lead, arsenic and selenium, a 20 ml volume of oil was extracted with a warm (not hot) mixture of 50 ml concentrated nitric acid plus 10 ml concentrated sulfuric acid by vigorous stirring for 16 hours.* Approximately 150 ml of distilled water were then added, and the mixture was extracted in a separatory funnel with two 100 ml portions of xylene to remove any undigested oils. The aqueous phase was diluted to 500 ml and analyzed by direct aspiration into the instrument.

For measurement of lead, an analogous extraction was carried out using nitric acid alone in order to avoid formation of lead sulfate. The acid extraction procedure did not afford recovery of the arsenic (triphenylarsine) and selenium (diphenylselenide) additives. Therefore, the amounts of these metals present in the spiked oils were determined by measurement of the volume additions of the stoichiometric compounds.

*Originally, the sulfuric acid was added to the nitric acid to aid in completely decomposing the oil by wet oxidation. Such an oxidation was extremely difficult to carry out routinely on a reasonable volume of fuel oil. However, it was found that the metal complexes were decomposed fairly readily and the metals were completely extracted into the aqueous acid after overnight reaction. Therefore, no further attempts were made to optimize this analysis.

SECTION 7

EXPERIMENTAL PROGRAM AND RESULTS

Experimental method evaluation runs were carried out in the source simulation apparatus, with simultaneous sample collection by two trains during each run. The evaluations correspond to one of four categories of tests, as follows:

- Sample collection and analysis evaluation runs (Runs 1-16, 18, 19) - variation in metal additives, sampling train nozzle material and impinger solutions, and sample work-up procedure.
- Field test (Run 17) - conducted at a coal-fired utility boiler.
- Evaluation of promulgated methods for Be and Hg (Runs 20, 21, 28).
- Testing the recommended procedure (Runs 22-27) - measurement of precision and accuracy for each metal additive from the results of replicate experiments.

A summary of the variables tested during these evaluation runs is given in Table 4. The stack conditions and amount of sample collected during each run are given in Table 5. Data sheets providing detailed information on metal additive recoveries for each of the collected samples are presented in Appendix B for the various evaluation tests.

The following sections describe the nature of the results for each series of evaluations and present the basis for following tests.

SAMPLE COLLECTION AND ANALYSIS EVALUATIONS

A summary of the experimental results, presented in detail in Appendix B, is given in Table 6. To provide a direct comparison of individual experiments, the results are normalized to a collected gas volume of one cubic meter (standard conditions). In each of the following cases, a set of experiments was planned, source simulation runs performed with collection of appropriate samples, and sample work-up and analysis conducted. Based upon the analytical results, a subsequent set of experiments was planned, and the process repeated.

- Runs 1-4

The major purpose of these runs was to check out the source simulation system and the ability to control gas temperature and flow rate. In addition, samples were collected to determine the blank level of metallic elements in the system and to evaluate the sample work-up procedure.

TABLE 4. SUMMARY OF EVALUATION RUN TEST VARIABLES

Run[1]	Additives[2]	Train	Samples[3]	Metals Analysed
1	None	A,B	F,AP,NP,I	NA
2	"	"	"	Cu,Fe,Mn,Pb
3	"	"	"	"
4	Mn	"	"	"
5	None	"	"	"
6	Co,Cr,Mn,Ni,V	"	--	NA
7	"	"	"	Cd,Co,Mn,Ni,V
8	None	"	F,F2,AP,NP,I	As,Cd,Co,Ni,Pb,Se,V
9	Cd,Co,Mn,Ni,Pb,V	"	"	Cd,Co,Mn,Ni,Pb,V
10	"	"	"	"
11	As,Cr,Mn,Se	"	F,F2,AP,NP,I	As,Cr,Mn,Se
12	"	"	"	"
13	As,Cd,Co,Cr,Mn,Ni,Pb,Se,V	"	--	NA
14	None	"	--	"
15	As,Cd,Co,Cr,Mn,Ni,Pb,Se,V	"	--	"
16	"	"	"	As,Cd,Co,Cr,Mn,Ni,Pb,Se,V
17	Source test	"	"	Mn,Pb,Se,V
18	As,Co,Mn,Ni,Pb,Se,V	A	F,AP,WP,NP,WI,I2	As,Co,Mn,Ni,Pb,Se,V
		B	F,APO.1NP,NP2,I	"
19	"	A	F,AP,0.1NP,NP2,0.1I,I2	"
		B	F,AP,0.1NP,NP2,I	"
20	Be	A	Method 103	Be
		B	Method 103[4]	"
21	Hg		Method 101	Hg
			Method 101[4]	"
22-25	As,Cd,Co,Cr,Mn,Ni,Pb,Se,V	A,B	F,AP,0.1NP,0	As,Cd,Co,Cr,Mn,Ni,Pb,Se,V
26-28	" + Be	A,B	"	" + Be
28	Be	A,B	"	Be

TABLE 4. (continued)

(1) Runs 1-16A utilized an all glass system, including the nozzle; Runs 16B-28 utilized a Method 5 train. In all cases, special glass cleaning procedures were used.

(2) For Runs 1-14, the levels added were $\sim 200 \mu g/m^3$, Runs 15 and 16, $\sim 100 \mu g/m^3$ and for Runs 18 and 19, $\sim 50 \mu g/m^3$. For Runs 22-28, additive levels were approximately: Se - $30 \mu g/m^3$; As, Cr, Mn - $40 \mu g/m^3$; Cd, Co, V - $50 \mu g/m^3$; Pb - $70 \mu g/m^3$; Ni - $90 \mu g/m^3$. In addition, Runs 26-28 contained $4 \mu g/m^3$ Be.

(3) Symbols represent individual analytical samples, as follows:

F	-	filter, extraction by 6N HNO_3
F2	-	second extraction by 6N HNO_3
AP	-	acetone probe wash
WP	-	water probe wash
NP	-	6N HNO_3 probe wash
0.1NP	-	0.1N HNO_3 probe wash
NP2	-	second probe wash with 6N HNO_3
I	-	impinger solutions and rinse with 6N HNO_3
WI	-	impinger solutions and rinse with distilled water
0.1I	-	impinger solutions and rinse with 0.1N HNO_3
I2	-	second impinger rinse with 6N HNO_3

(4) Probe washings and combined impinger catch and rinse separately analysed.

TABLE 5. SUMMARY OF EVALUATION RUN CONDITIONS

Run No.	Stack Conditions					Sampling Conditions			
						Train A		Train B	
	Temp. (°C)	Velocity (m/sec)	Volume (SCM @ STP)[4]	CO_2 (%)	H_2O (%)	Rate (a m^3/min)	Volume (SCM @ STP)[4]	Rate (m^3/min)	Volume (SCM @ STP)[4]
1	220	5.27	351.17	0.7	2.2	0.013	0.86	0.011	0.745
2	125	10.84	923.29	1.2	1.2	0.033	1.824	0.033	1.759
3	120	11.77	971.52	0.8	1.2	0.033	1.724	0.033	1.726
4	120	10.53	908.76	0.7	1.0	0.035	1.779	0.035	1.753
5	145	9.51	896.81	0.7	0.9	0.025	1.578	0.025	1.574
6	145	10.13	955.15	0.7	1.9	0.026	1.717	0.026	1.710
7	145	9.82	(1)	0.7	1.7	0.018	1.593	0.031	1.641
8	155	9.98	1499.88	0.7	1.8	0.014	1.589	0.015	1.632
9	155	10.97	1586.26	0.7	1.6	0.015	1.618	0.016	1.690
10	150	10.78	1569.04	0.7	1.8	0.015	1.614	0.016	1.694
11	155	10.49	1516.85	0.7	2.1	0.007	1.495	0.007	1.534
12	150	10.44	1676.43	0.7	2.4	0.013	1.518	0.012	1.406
13	140	10.82	1794.67	0.7	2.1	0.016	1.796	0.015	1.709
14	140	10.58	1602.60	0.7	2.5	0.015	1.697	0.015	1.718
15	135	10.72	1627.44	0.7	2.7	0.016	1.737	0.017	1.709
16	135	10.53	877.98	0.7	1.9	0.032	1.712	0.033	1.752
17	175	13.00	599,122[2]	13.4	7.0	0.014	0.853	0.015	0.843
18	120	10.34	1760.09	0.7	2.5	0.014	1.553	0.013	1.530
19	125	10.44	1727.75	0.7	--	0.015	1.591	0.014	1.558
20	115	10.45	2718.72	0.7	1.0	0.014	2.359	0.014	2.409
21	115	10.46	1809.65	0.7	1.9	0.014	1.642	0.014	1.591
22	115	9.96	1757.57	0.7	0.4	0.015	1.692	0.015	1.737
23	115	9.70	1703.82	0.7	1.0	0.014	1.643	0.014	1.659
24	115	9.84	1733.18	0.7	--	0.015	1.732	0.015	1.713
25	120	9.91	1727.52	0.7	1.2	0.014	1.671	0.014	1.636
26	110	9.23	1686.65	0.7	0.5	0.014	1.640	0.014	1.645
27	110	9.29	(3)	0.7	0.7	0.014	1.590	0.013	1.565
28	125	9.76	2467.85	0.7	0.9	0.022	2.431	0.022	2.408

(1) Train A - 1309.06; Train B - 1018.16

(2) Field sample

(3) Train A - 1679.80; Train B - 1705.77

(4) STP - 21°C (70°F) and 760 mm Hg (29.92 in Hg)

TABLE 6. SUMMARY OF SAMPLE COLLECTION AND ANALYSIS EVALUATIONS

Run No.	Element - micrograms (A = actual, F = found, % = percent recovery)																							
	As			Cd			Co			Cr			Mn			Ni			Pb			Se			V		
	A	F	%	A	F	%	A	F	%	A	F	%	A	F	%	A	F	%	A	F	%	A	F	%	A	F	%
2A			Cu –	0	13	–			Fe –	0	74	–	0	5	–				0	66	–						
2B				0	16	–				0	56	–	0	4	–				0	66	–						
3A			Cu –	0	7	–			Fe –	0	50	–	0	3	–				0	49	–						
3B				0	6	–				0	>41	–	0	>2	–				0	54	–						
4A			Cu –	0	11	–			Fe –	0	38	–	223	158	71				0	49	–						
4B				0	10	–				0	41	–	223	148	66				0	44	–						
5A				0	5	–	0	2	–				0	2	–	0	6	–							0	<16	–
5B				0	2	–	0	1	–				0	2	–	0	7	–							0	<10	–
7A				194	207	107	334	316	94				205	182	88	276	283	103							211	211	100
7B				200	214	107	344	334	97				211	217	102	285	310	110							218	230	106
8A	0	1	–	0	5	–	0	6	–							0	6	–	0	16	–	0	2	–	0	18	–
9A				185	222	120	183	224	120				183	232	127	192	267	139	203	273	134				218	245	113
10A				183	214	116	182	219	121				182	236	129	191	223	116	202	260	127				216	183	84
11A	179	94	52							200	193	97	151	196	131							183	79	53			
11B	184	72	39							205	99	49	155	196	127							188	76	39			
12A	208	71	33							245	185	76	165	193	116							213	93	44			
12B	193	96	50							227	180	79	153	188	123							197	106	54			
16A	102	19	19	80	98	118	115	127	112	94	84	89	77	89	116	124	123	99	74	89	120	104	52	49	73	62	85
16B	105	18	18	82	94	115	118	108	92	97	123	126	79	85	108	127	109	85	76	93	123	106	44	42	77	65	85
18A	78	19	23				86	53	60				64	59	92	78	50	64	71	68	96	78	20	26	49	48	98
18B	76	38	50				85	80	94				63	92	146	76	80	105	70	117	167	77	35	45	58	61	105
19A	92	51	55				77	76	99				76	89	117	105	92	88	84	100	119	93	26	28	70	67	96
19B	90	44	49				75	73	97				74	88	119	103	96	93	82	105	128	91	32	35	69	74	107

The attainment of high gas temperatures, i.e., in excess of 200°C (400°F) could be obtained by a substantial reduction in dilution air, corresponding to a linear flow rate of ∿5 m/sec (∿17 ft/sec). For a more normal duct flow of ∿10 m/sec (∿35 ft/sec), gas temperatures of 110-150°C (230-300°C) could be obtained. This latter set of conditions was selected as most representative of stationary source conditions and was employed throughout the tests.

Filter, acetone probe wash, nitric and probe wash and impinger samples for Runs 2, 3 and 4* were separately analysed for Cu, Ni, Mn and Pb to determine the levels of these elements introduced by the system. The results, given in Appendix B, pages 1-3, indicate low levels of Cu (5-15 $\mu g/m^3$) and Mn (2-5 $\mu g/m^3$) and high levels of Fe (40-75 $\mu g/m^3$) and Pb (45-65 $\mu g/m^3$) tended to be equivalently distributed among the filter, probe washes and impinger samples. The levels obtained were not unreasonable as a system background. Pb, however, was almost entirely found in the filter sample. It is possible that a contaminant source of lead may have been present in the pilot plant and introduced in the dilution air. This was not specifically tested, however.

The Mn data for Run 4 provided a 65 percent recovery, with almost all Mn present in the filter sample.

- Runs 5-7

This series of runs was conducted to evaluate recoveries for elements having stable oxides (Cd, Co, Mn, Ni and V). Run 5 was a blank and Runs 6 and 7 included the metals of interest at levels corresponding to ∿200 $\mu g/m^3$. The results are presented in Appendix B, pages 4-5. The Run 5 blank system data were all very low (Co and Mn ∿2 $\mu g/m^3$, Cd and Ni ∿4 to 7 $\mu g/m^3$). Vanadium was below the detectable limit which, for these analyses, was 10-15 $\mu g/m^3$. Run 7 yielded recoveries near 100 percent for all elements with the majority of each element (∿90 percent or more) found in the filter sample. The nitric acid probe wash samples contained about half the level of metal found in the initial acetone probe wash.

- Runs 8-10

Run 8 represented a blank run analysed for As, Cd, Co, Ni, Pb, Se and V. Runs 9 and 10 were comparable to Run 7, but also included Pb. Only the A train samples were analysed, with the results given in Appendix B, pages 6-8. Blank levels were again low for Cd, Co and Ni, and also for As and Se (<5 $\mu g/m^3$) and were somewhat higher for Pb and V (15-20 $\mu g/m^3$), as before. Runs 9 and 10 systematically showed high recoveries (120 to 130 percent) for all elements. This possibly can be explained by an error in the amount of metal added to the fuel. For these tests, the

*Run 4 included an intentional addition of Mn corresponding to 233 μg Mn/m^3.

filters were twice extracted with 6N HNO_3. Metal contents in the second extraction were only 1 to 5 percent of the amounts present in the first extraction. It is concluded that a single extraction is adequate.

- Runs 11-16

Runs 11 and 12 included new additives As, Se and Cr, as well as Mn. Runs 13, 15 and 16 included all nine metals as additives*, with Run 14 being a blank run. The detailed results for Runs 11 and 12 are presented in Appendix B, pages 9 and 10. Recoveries were somewhat high (∿125 percent) for Mn and low (∿75 percent) for Cr. About 15 percent of the Mn was found in the impingers, contrary to earlier findings. No explanation can be offered for this result or for the somewhat low recoveries for Cr.

Very low recoveries were obtained for As and Se (30-50 percent). Of the amount recovered, most was present in the filter sample.

As a result of these low recoveries for As and Se, a series of laboratory tests were conducted to determine how much of the loss could be attributed to the analytical work-up prior to measurement. These evaluations are described in detail in the next section (V, B).

Because of the special studies required due to the poor As and Se recoveries, samples from Runs 13-15 were not analysed. Run 16, employing a glass nozzle for Train A and a stainless nozzle for Train B, was analysed for all metals, expected to be present at levels of ∿100 $\mu g/m^3$. The results are given in Appendix B, page 11. With a few exceptions, recoveries were generally close to 100 percent. As and Se recoveries were very low (20 and 45 percent, respectively) and the recovery for V was lower (65 percent) than for other tests. Other deviations from good recoveries were generally attributable to one sample giving a high result. In a few cases, this was felt to be due to contamination from employing a storage container that had not been thoroughly cleaned. The high recovery of Cr in the nitric acid probe wash is attributed to pick-up from the stainless steel nozzle.

From these experiments, it is concluded that the analytical methods were generally satisfactory for all additive metals except As, Se and maybe V. Recoveries for the two trains were generally comparable. For these runs, the sampling train clean-up procedure was considerably more difficult than for the usual Method 5 train, requiring special glass cleaning before sampling, disconnecting the nozzle prior to probe clean-up, collection of impinger solutions and use of 6N HNO_3 for probe and impinger washes. Simplification would be desirable.

*Runs 15 and 16 additives corresponded to ∿100 $\mu g/m^3$.

Goals for further method evaluation studies include measurements of the effectiveness of probe and impinger washing by separately recovering a second wash, comparing the suitability of distilled water and 0.1N HNO_3 to 6N HNO_3 as an impinger solution and washing agent, and providing further measurements of recoveries and distribution between the various collected samples.

- Runs 18 and 19

As a safety measure, it would be desirable to avoid using strong acid probe wash and impinger solutions. Based upon the results of Run 16B, Cr is picked up from the stainless nozzle during probe washing with 6N HNO_3. If a water probe wash could be used, it would be unnecessary to remove the sampling nozzle before carrying out the probe wash. It is quite easy to break the glass probe liner during this disassembly of the nozzle. Therefore, Runs 18 and 19 were carried out with Method 5-type sampling trains, with Pb, Mn, Ni, Co, V, Se and As additives to the fuel oil. The B train for these runs utilized 6N nitric acid impinger solutions as for all previous runs. After sampling, the glassware in the train was rinsed with acetone followed by two separate 6N nitric acid rinses. Each of these solutions was separately analysed to determine the rinsing efficiency of the various solutions. The A train in Runs 18 and 19 employed distilled water and 0.1N nitric acid in the impingers, respectively, for comparison to the 6N nitric impinger solutions in the B train. The clean-up procedure utilized the same distilled water and 0.1N nitric solutions for the first rinse followed by 6N HNO_3 for the second rinse. The experimental results for these runs are given in Appendix B, pages 12 and 13.

The B train of Run 18 reveals considerably higher than expected recoveries for Pb, Mn, Ni and Co. It is probable that this sample was contaminated, possibly through the use of a dirty container to collect one of the glassware rinse solutions. The A train shows good recoveries for the transition metals and Pb, with the major fraction of these elements collected on the filter. Recoveries for As and Se were only about 25 percent.

The analytical results for Run 19 show excellent agreement between A and B trains. Recoveries were excellent except for As and Se. No metal was found in the second (6N) nitric acid probe wash or impinger of the A train. It is concluded that the use of 0.1N nitric acid for impinger solutions and glassware clean-up leads to complete sample recovery.

RECOVERY OF ARSENIC AND SELENIUM FROM SAMPLING TRAIN AND OIL SOLUTIONS

Initial source simulation tests using oil containing triphenyl arsenic and diphenyl selenide additives gave very low recoveries of both elements based upon the amount of additive used.

A number of laboratory experiments were conducted to define the best procedures for measuring selenium and arsenic. Our tentative method for both these elements was the hydride evolution - atomic absorption technique. This method involves adding 15 ml of concentrated HCl to a 30 ml aliquot of the As or Se containing solution in a closed vessel and then dropping a sodium borohydride pellet into the solution. The hydride (arsine or hydrogen selenide) evolved is blown into the AA flame in a stream of argon. Fernandez[3] studied the effect of varying the concentration of hydrochloric acid in the hydride generation solution and found that for arsenic maximum response was obtained with hydrochloric acid concentrations in the range 2 to 6 molar, while for selenium the maximum response was obtained only when the hydrochloric acid concentration was at least 5 molar. For the present work, hydrochloric acid concentrations of 3 molar and 6 molar were used for arsenic and selenium to make certain that the generation solution was sufficiently acidic.

Because the nitric acid that is used as the solvent in the present tests is a good oxidizing agent, and thus might interfere with the hydride reduction, a series of tests were carried out in which different concentrations of nitric acid were spiked with appropriate amounts of arsenic and selenium calibration standards, and then analyzed via the hydride evolution procedure. The results of those tests are given in Table 7.

These data indicate that nitric acid concentrations much in excess of 0.5 to 1 mol/l in the sample colution will have a depressive effect on the analysis of arsenic and selenium using the hydride evolution method.

In order to determine how much of the apparent loss could be attributed to analytical work-up prior to measurement, a series of tests was conducted in which both organic and inorganic forms of these elements were subjected to different work-up conditions. The inorganic species were prepared from the respective atomic absorption standards, while the respective organo-additives were dissolved in benzene to provide a working solution. The benzene was evaporated before other reagents were added. Known quantities of arsenic and selenium species were subjected to the reaction conditions listed below.

a. Portions of the inorganic and organic species were mixed with 500 ml of 6N nitric acid, and the resulting solution evaporated and treated as an impinger solution by the procedure shown in Figure 4.

b. Portions (2 ml) of the inorganic and organic species were treated with 25 ml bromine water for 15 minutes, after which 500 ml of 6N nitric acid were added and the solution treated as in (a) above.

TABLE 7. EFFECT OF NITRIC ACID ON ARSENIC AND SELENIUM HYDRIDE GENERATION

HNO_3 Conc. in Sample Solution (mol/l)	Sensitivity (abs. units/microgram of element)	
	Arsenic*	Selenium≠
0	0.43	0.085
0.02	--	0.080
0.1	0.46	--
0.5	0.45	0.072
1	0.35	0.046
2	0.20	--
4	0.065	0.040
6	--	0.040

* As analysis procedure utilizes 30 ml sample plus 10 ml conc. HCl.

≠ Se analysis procedure utilizes 20 ml sample plus 20 ml conc. HCl.

c. Portions (2 ml) of the inorganic and organic species were treated with 25 ml of 30% hydrogen peroxide for 15 minutes after which 500 ml of 6N nitric acid were added and the solution treated as in (a) above.

d. The evaporation of nitric acid from solutions containing inorganic species described in (a) above was repeated using a distilling flask and condenser to catch the distillate.

e. Portions of the inorganic species were applied to glass fiber filters and extracted for 60 minutes with nitric acid (as in Figure 4) except that the extraction was carried out at the boil in a flask fitted with a Friedrich condenser to give complete reflex. The entire solution was diluted for analysis; the nitric acid concentration in the generation solution was 0.2N.

f. Portions of the organic species were applied to glass fiber filters. The spiked filters were fused with sodium peroxide (Na_2O_2), the resulting melt was dissolved in water and neutralized with nitric acid, and the solution was analyzed using the borohydride procedure.

The results of these experiments are given in Table 8. These data lead to the following conclusions regarding extraction and digestion of samples containing arsenic and selenium.

- Inorganic selenium is retained during evaporation of the nitric acid solvent while inorganic arsenic is not. However, inorganic arsenic is retained if acid digestions are carried out under total reflux.

- Recovery of arsenic and selenium from the tri- and diphenyl compounds is extremely difficult using commonly accepted chemical decomposition techniques, since even an oxidative, alkaline fusion gave only a 25% recovery.

- Use of halogen oxidants such as bromine will result in substantial losses of inorganic selenium.

Thus, the nitric acid collection procedure, modified to include measurement of arsenic prior to evaporation of the acid, is applicable to inorganic arsenic and selenium. However, it is not likely to be useful for aromatic organometallic compounds unless different oxidation conditions, such as oxygen plasma ashing ("low temperature ashing"), can be utilized, since the hydride evolution method works only with the inorganic species.

TABLE 8. RECOVERY OF ARSENIC AND SELENIUM FROM PRETREATMENT PROCEDURES

Procedure No.	Org/ Inorg	Arsenic			Selenium		
		Added (µg)	Found (µg)	% Rec	Added (µg)	Found (µg)	% Rec
a (evap)	inorg	200	138	69	200	210	105
	org	200	<5	<3	200	<12	<6
		10	<.25		10	<.5	
b (Br_2 water)	inorg	200	130	65	200	2	1
	org	200	<5	<3	200	<12	<6
		10	<.25		10	<.5	
c (H_2O_2)	inorg	200	117	59	200	205	103
	org	200	<5	<3	200	<12	<6
		10	<.25		10	<.5	
d (dist.)	inorg-residue	200	165	83	not added		
	condensate		<5	<3			
e (reflux)	inorg	100	98	98	100	93	93
f (fusion)	org	200	50	25	200	32	16

The foregoing data indicates the difficulty in decomposing and digesting the phenyl arsenic and selenium compounds. As would be expected, analysis of the spiked fuel oils using the nitric acid digestion and AAS measurement procedures described above did not show an appreciable recovery of the amounts of arsenic and selenium added.

Based on the preceding analytical results, a plausible explanation for the poor As and Se recoveries in source simulation runs is that the triphenyl arsine and diphenyl selenium are not completely oxidized during oil combustion in the source simulation apparatus. To test this possibility, sections of a filter (not previously analyzed) from Run 15, in which both As and Se were present as additives to the oil, were analyzed for the presence of As and Se organic compounds in the mass spectrometer.

The filter sample yielded several As-containing fragments ($C_6H_5As^+$, $C_{12}H_8As^+$, $C_{18}H_{15}As^+$) providing good evidence for the presence of non-combusted triphenyl arsine. Selenium compounds were less prominent (about one-tenth as intense as the As compounds) and contained nitrogen indicating partial combustion. The major fragments were $C_6H_5NO\ Se^+$ and $C_6H_5NO_2Se^+$.

The poor recoveries for As and Se are, therefore, attributed to incomplete dissociation and combustion of the organic compound additives.

FIELD EVALUATION OF SAMPLE COLLECTION

Field sampling at stationary sources expected to have trace hazardous metals in their emissions was one of the original program goals. The purpose of the field sampling was to test the procedure under actual field conditions to determine problems or shortcomings not likely to develop during laboratory tests. Also, the collected samples were analysed for several metals to determine the relative distribution of metals among the various samples from train clean-up. A determination of the recoveries was, of course, not possible due to the lack of any reference data for this source.

Two sampling runs (identified as Run 17) were carried out simultaneously in the breeching to the stack at the coal-fired boiler. Glassware was initially pre-cleaned by the recommended procedure (Section IV, B). Six $\underline{N}$ HNO_3 was used for impinger solutions and for probe and impinger rinsing. The stainless nozzle was removed prior to the nitric probe wash. The run conditions are given in Table 5.

Several comments were made by the field sampling team regarding the sampling procedure, as follows:

- It is very difficult to safely handle 6$\underline{N}$ HNO_3 for changing impingers and for the glassware rinse. Besides the danger from spillage to personnel, these would be a long-term impact on equipment and scaffolding.

- For probe cleaning with 6N HNO_3, it was necessary to remove the nozzle, increasing the likelihood of damage to the glass probe.

- The glass pre-cleaning procedure is almost impossible to use in the field. (Where does one dispose of the 8N HNO_3 soak solution?)

As a result of these comments, further laboratory evaluation tests were planned (Runs 18 and 19, described in Section VII, A) to evaluate the use of 0.1N HNO_3, hopefully precluding the need for nozzle removal during probe cleaning.

The field samples were analysed for several elements, with the results given in Table 9. With the exception of V, the two trains yield equivalent results. Very little metal is collected by the second nitric acid extraction. Not very much metal is collected by the nitric acid probe wash or in the impingers for Mn, As or V. About 10 percent of the Pb, however, is found in both the impingers and the nitric acid probe wash.

EVALUATION OF PROMULGATED METHODS FOR BERYLLIUM AND MERCURY

Beryllium (Run 20, Run 28)

Run 20 was carried out according to EPA Method 104* for beryllium emissions from stationary sources. Samples were collected simultaneously with two duplicate trains. The EPA specified clean-up procedure was followed strictly for one train, with the impinger solutions and the probe washes from the other train kept separate to get some idea of the distribution of Be within the trains. As a safety measure, a flue gas concentration of beryllium corresponding to about one-tenth the TLV for occupational exposure was selected for Run 20; consequently, the quantities of beryllium captured in the train were only slightly greater than the limit of detectibility (about 0.03μg). Most of the beryllium was found on the filter (see Table 10). However, there is an indication that some beryllium was present in the impingers. It should be understood that the Be measurements were not of high accuracy because of the small quantity of material involved.

Four further tests were conducted at a tenfold higher concentration of Be as part of the replicate precision and accuracy experiment series (Section VII, D). For these, all samples were combined according to the work-up procedure shown in Figure 4. The results are also given in Table 10.

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*Federal Register 38, 8846-8850 (April 6, 1973).

TABLE 9. METAL CONTENT OF STACK SAMPLES COLLECTED AT A COAL-FIRED UTILITY BOILER

Sample	Metals (μg)							
	Mn		Pb		Se		V	
	A	B	A	B	A	B	A	B
Filter (1st extraction)	6	8	36	47	5	5	22	32
Filter (2nd extraction)	1	2	2	5	1	<1	2	<2
Acetone probe wash	12	15	36	24	14	20	11	26
6N HNO_3 probe wash	2	2	7	10	<1	<1	<2	<2
6N HNO_3 impingers and wash	4	2	7	8	3	9	<2	<2
Total	25	29	88	94	23	35	39	64

TABLE 10. METHOD EVALUATION FOR BERYLLIUM

A. Beryllium Analysis by Method 104

Sample	Amount ($\mu g/m^3$)			
	Run 20		Run 28	
	Train A	Train B	Train A	Train B
Expected	0.38	0.39	5.4	5.4
Found				
Filter	0.21	0.27		
Probe	0.03	0.08		
Impinger		0.08		
Total	0.24	0.45	5.4	5.4
Percent Recovered	63	115	100	100

B. Beryllium Analysis during Replicate Precision and Accuracy Experimental Runs

Run No.	Amount ($\mu g/m^3$)		Percent Recovery
	Expected	Found	
26A	3.2	3.7	116
26B	3.2	3.7	116
27A	3.1	3.8	123
27B	3.1	3.8	123

Consequently, a subsequent Method 104 (Run 28) experiment was carried out at a tenfold increase in Be concentration. The results, also given in Table 10, show excellent recoveries. The samples from Run 28 were combined, as called for by the Method 104 work-up procedure. Therefore, no comment can be made about the distribution of Be within the sampling train.

For comparison, levels of Be comparable to those present in Run 28 were added to two of the runs during the precision and accuracy replicate experiments described in the next section. The major difference from Method 104 was use of a quartz fiber filter and 0.1N HNO_3 impinger and wash solutions. Samples were combined and analysed according to the work-up procedure shown in Figure 4. The results, also given in Table 10, indicate very good recoveries. It can be concluded that the method recommended herein for other trace metals is equally suitable for beryllium.

Mercury

An evaluation (Run 21) of EPA Method 101* for measuring mercury in air streams was carried out by burning an oil spiked with mercury naphthenate, and sampling with two identical trains. Method 101 utilizes 0.1N iodine monochloride in aqueous hydrochloric acid for the impinger solutions and for washing out the sampling train after collection. The EPA specified clean-up procedure was followed strictly for the A train, while the impinger solutions and the probe washes from the B train were analysed separately to get some idea of the distribution of Hg within the train. The results are given in Table 11.

The analyses were carried using a "cool vapor" apparatus similar to that described by Hatch and Ott . This apparatus incorporates a peristaltic pump, a smog-bubbler reaction vessel and a 6 inch optical cell, and is coupled to a Perkin-Elmer Model 303 AA Spectrophotometer equipped with recorder readout.

The data for Run 21 indicate good recoveries of mercury using Method 101, although the duplicate measurement for train A indicated very poor precision.

The data for the B train indicates that nearly all of the mercury is collected in the impingers, as expected.

Because Method 101 specifies only that the analysis of the sample solution is to be repeated until "reproducible" peak heights are obtained, it was deemed appropriate that a brief study of the precision of Method 101 be compared with other accepted procedures.

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*Federal Register 38, 8835-8840 (April 6, 1973).

TABLE 11. METHOD 101 EVALUATION FOR MERCURY

Sample	Amount ($\mu g/m^3$)	
	Train A*	Train B
Expected	0.70	0.70
Found		
Filter	<0.01	<0.01
Probe	0.70, 1.71	0.13
Impinger		1.09
Total	0.70, 1.71	1.24
Percent recovery	100, 245	175

*Duplicate measurements were made of the combined probe and impinger solutions.

As a result, an evaluation was made of the precision and accuracy of several analysis procedures for mercury utilizing a freshly prepared aqueous mercuric nitrate standard solution and the above-described apparatus. The procedures tested were:

a. The Method 101 procedure: reduction in alkaline solution with hydroxylamine; once-through vapor sparing; measurement of maximum absorbance;

b. Method 101 chemistry with the apparatus modified to permit recirculation of sparge gas; measurement of maximum absorbance;

c. "Hatch and Ott" Procedure: reduction in acid solution with stannous sulfate; recirculation of sparge gas; measurement of maximum absorbance.

The results of these tests are given in Table 12. The above data indicate that the best precision and accuracy if obtained from the acidic reduction procedure. Unfortunately, this procedure is incompatible with the use of iodine monochloride scrubbing solutions, as the end result would be the formation of mercuric iodide rather than elemental mercury.

For the alkaline reduction, the recirculating procedure yields somewhat less scatter in data with equivalent accuracy compared to the EPA Method 101, single pass procedure. On the basis of these tests, it is recommended that in order to assure reasonable precision and accuracy, at least ten measurements be averaged for Hg analysis by the EPA Method 101 procedure.

STATISTICAL TESTING OF THE RECOMMENDED PROCEDURE

On the basis of the evaluations described in the preceeding sections, a series of experiments were conducted to determine the precision and accuracy of trace metal sampling and analysis. Six runs with duplicate trains were made, using the following sampling procedure:

- Glassware precleaning - overnight soak in alconox-water, hot water rinse, 8N HNO_3 rinse, acetone and distilled water rinse just prior to train assembly.

- Impinger solution - 0.1N HNO_3.

- Glassware rinse - acetone followed by 0.1N HNO_3.

- Sample treatment - all samples combined for analysis (see Figure 4).

TABLE 12. SUMMARY OF RESULTS FOR SEVERAL MERCURY MEASUREMENT PROCEDURES

Method	Hg Added (µg)				
	0	0.05	0.10	0.20	0.50
a. EPA Method 101 (Alkaline, single pass)					
No. of Measurements	12	8	10	7	3
Avg. Mass Found (µg)	0.0073	0.034	0.101	0.216	0.483
Std. Dev.	0.0084	0.027	0.034	0.058	0.053
Coef. of Var. (%)	115	79	34	27	11
b. Modified EPA (Alkaline, recirculating)					
No. of Measurements	9	8	6	6	--
Avg. Mass Found (µg)	0.0044	0.041	0.108	0.201	--
Std. Dev.	0.0011	0.019	0.027	0.040	--
Coef. of Var. (%)	25	46	25	20	--
c. Acidic Evolution (Recirculating)					
No. of Measurements	3	3	3	3	--
Avg. Mass Found (µg)	0.0061	0.045	0.095	0.204	--
Std. Dev.	0.0008	0.002	0.003	0.014	--
Coef. of Var. (%)	13	4	3	7	

To provide a known metals content in the combustion gas stream of approximately 50$\mu g/m^3$, the various organometallic additives were combined with xylene to form a fuel concentrate. About one part of concentrate was added to 20 parts fuel in quantities sufficient for two runs. A portion of the fuel concentrate was analysed by the procedure described in Section VI, F to determine actual metals content. The results are given in Table 13. For any given experiment, the expected metals content was determined as follows:

$$\text{metal expected } (g/m^3) = \text{metal in concentrate } (g) \times \frac{\text{weight concentrate } (g)}{\text{weight fuel + concentrate } (g)}$$

$$\times \frac{1}{\text{combustion volume } (m^3)}$$

Combustion volume was determined from actual stream velocity (based on Pitot tube measurements during the run) multiplied by stack cross section and run time and corrected to standard conditions. Based upon the experimental run conditions, most metals were present in the stack gas at expected concentrations of 30-50$\mu g/m^3$; Se, As and Ni were somewhat higher, in the range 60-90$\mu g/m^3$.

To permit an evaluation of the developed procedure for beryllium, for comparison to the Method 104 procedure, beryllium acetylacetonate was added to the fuel concentrate used for Runs 26 and 27 in amounts corresponding to an expected stack gas concentration of 3$\mu g/m^3$. An aliquot of the final solution (Figure 4) was taken for beryllium analysis by atomic absorption. The results are given in Table 10B.

The experimental conditions for the evaluation runs are given in Table 5, with analytical results presented in Table 14. Recoveries are generally quite good except for As and Se (low) and Pb (high). A statistical summary of the data is given in Table 15 and Figure 5.

The reproducibility of the method is quite good for most metals, with a precision of 7-11 percent, corresponding to 3-5$\mu g/m^3$. Arsenic and selenium are less precise, corresponding to 21 and 15 percent (9 and 5$\mu g/m^3$), respectively. Very good accuracy is observed for Co, Mn and Ni (2-6 percent, 1-3$\mu g/m^3$), with acceptable levels observed for Cd, Cr and V (13-16 percent, 5-7$\mu g/m^3$). In contrast, the accuracy of the method for Pb, As and Se is poor, with Pb being 30 percent (16$\mu g/m^3$) high and As and Se being about 30 and 50 percent (20 and 30$\mu g/m^3$) low.

The high values for Pb cannot be explained. The concentration of Pb in the fuel concentrate was separately analysed (see the oil analysis procedure described in Section VI, F). It is possible that some error occurred during this analysis, leading to a low value for the expected lead concentration. Further work should be carried out to identify the

TABLE 13. METALS CONTENT IN FUEL CONCENTRATE

Metal	Micrograms Metal/Gram Concentrate
As	307.7
Be	11.5
Cd	214.6
Co	257.8
Cr	179.6
Mn	172.6
Ni	425.9
Pb	253.2
Se	304.6
V	200.3

TABLE 14. RESULTS OF REPLICATE EXPERIMENT SERIES

Element	RUN NUMBER								
	22A	23A	23B	24A	24B	26A	26B	27A	27B
As - Expected (µg/m³)	63.6	58.8	58.8	58.5	58.3	68.6	68.7	67.5	66.5
- Found (µg/m³)	37.8	51.9	42.4	44.6	32.6	51.4	57.6	34.5	34.1
- Recovery (%)	59.4	88.3	72.1	76.2	55.9	74.9	83.8	51.1	51.3
Cd - Expected (µg/m³)	44.3	41.0	41.0	40.8	40.7	47.9	47.9	47.1	46.4
- Found (µg/m³)	51.1	47.8	48.8	52.8	52.8	52.8	50.5	50.3	50.5
- Recovery (%)	115.4	116.6	119.0	129.4	129.7	110.2	105.4	106.8	108.8
Co - Expected (µg/m³)	53.3	49.3	49.3	49.0	48.9	57.5	57.5	56.6	55.7
- Found (µg/m³)	53.2	51.7	51.2	52.5	55.5	52.4	51.7	51.6	46.0
- Recovery (%)	99.8	104.9	103.9	107.1	113.5	91.0	89.9	91.2	82.6
Cr - Expected (µg/m³)	37.1	34.3	34.3	34.1	34.0	40.1	40.1	39.4	38.8
- Found (µg/m³)	44.3	41.7	42.2	34.6	44.4	42.7	44.1	40.9	38.3
- Recovery (%)	119.4	121.6	123.0	101.5	130.6	106.5	110.0	103.8	98.7
Mn - Expected (µg/m³)	35.7	33.0	33.0	32.8	32.7	38.5	38.5	37.9	37.3
- Found (µg/m³)	36.4	36.8	37.7	37.2	39.2	38.1	37.7	37.4	37.7
- Recovery (%)	102.0	111.5	114.2	113.4	116.9	99.0	97.9	98.7	101.1
Ni - Expected (µg/m³)	88.0	81.4	81.4	80.9	80.7	95.0	95.0	93.5	92.1
- Found (µg/m³)	99.3	98.6	94.7	92.9	99.8	94.5	94.8	90.6	81.2
- Recovery (%)	112.8	121.1	122.4	114.8	123.7	99.5	99.8	96.9	88.2
Pb - Expected (µg/m³)	52.3	48.4	48.4	48.1	48.0	56.5	56.5	55.6	54.7
- Found (µg/m³)	70.3	66.3	71.7	65.8	67.1	70.1	66.3	63.8	66.5
- Recovery (%)	134.4	137.0	148.1	136.8	139.8	124.1	117.4	114.8	121.6
Se - Expected (µg/m³)	62.9	59.2	58.2	57.9	57.7	67.9	68.0	66.9	65.8
- Found (µg/m³)	30.7	28.9	29.8	32.9	33.3	43.2	37.3	31.3	24.8
- Recovery (%)	48.8	48.8	51.2	56.8	57.7	63.6	54.9	46.8	37.7
V - Expected (µg/m³)	41.4	38.3	38.3	38.1	38.0	44.7	44.7	44.0	43.3
- Found (µg/m³)	48.5	45.6	46.4	49.1	46.7	47.0	45.6	44.0	45.4
- Recovery (%)	117.2	119.1	121.2	128.9	122.9	105.2	102.0	100.0	104.9
Be - Expected (µg/m³)						3.2	3.2	3.1	3.1
- Found (µg/m³)						3.7	3.7	3.8	3.8
- Recovery (%)						115.6	115.6	122.6	122.6

TABLE 15. PRECISION AND ACCURACY OF NINE REPLICATE EXPERIMENTS

Element	Expected	Found	Accuracy		Precision	
	($\mu g/m^3$)	($\mu g/m^3$)	$\mu g/m^3$	%	$\mu g/m^3$	%
As	63.3	43.1	-20.1	-31.9	8.9	20.6
Cd	44.1	51.0	6.9	15.6	4.0	7.8
Co	53.0	52.1	- 0.9	- 1.7	5.3	10.2
Cr	36.9	41.6	4.7	12.7	4.1	9.9
Mn	35.5	37.7	2.2	6.2	2.8	7.3
Ni	87.6	84.2	- 3.4	- 3.9	9.6	11.4
Pb	52.1	68.0	15.9	30.5	5.9	8.7
Se	62.6	32.4	-30.2	-48.2	4.7	14.5
V	41.2	46.7	5.5	13.3	4.3	9.2
Be	3.2	3.8	0.6	18.8	0.1	3.4

analytical step leading to high lead values. For the present, lead analyses by the recommended method must be considered as conservative estimates.

Arsenic and selenium recoveries are low and variable. Based upon the results of special laboratory tests (Section VII, B), it appears that the low recoveries are due to incomplete combustion of the organometallic additives for these metals, with only the inorganic fraction being analysed. Also, it is possible that As and Se may exist in a form that is not collected by the proposed sampling train and procedure. In any case, the recommended method is not suitable for As and Se.

SUMMARY

The program goals have substantially been met for Cd, Co, Cr, Mn, Ni, Pb and V, with common sample collection, pretreatment and analysis for all metals. The recommended sampling procedure is similar to Method 5, with only minor modifications with respect to the sampling train configuration and sample recovery. Based upon replicate analyses, a precision of about 10 percent is achieved for all metals (excepting As and Se) with an accuracy of 10 percent Co, Mn and Ni, 15 percent for Cd, Cr and V, and 30 percent for Pb. The method is not useful for As and Se on the basis of poor recoveries for the replicate experiments. Further work is indicated for these two elements.

The Reference Method for determining Cd, Co, Cr, Mn, Ni, Pb and V emissions from stationary sources is given in Appendix C.

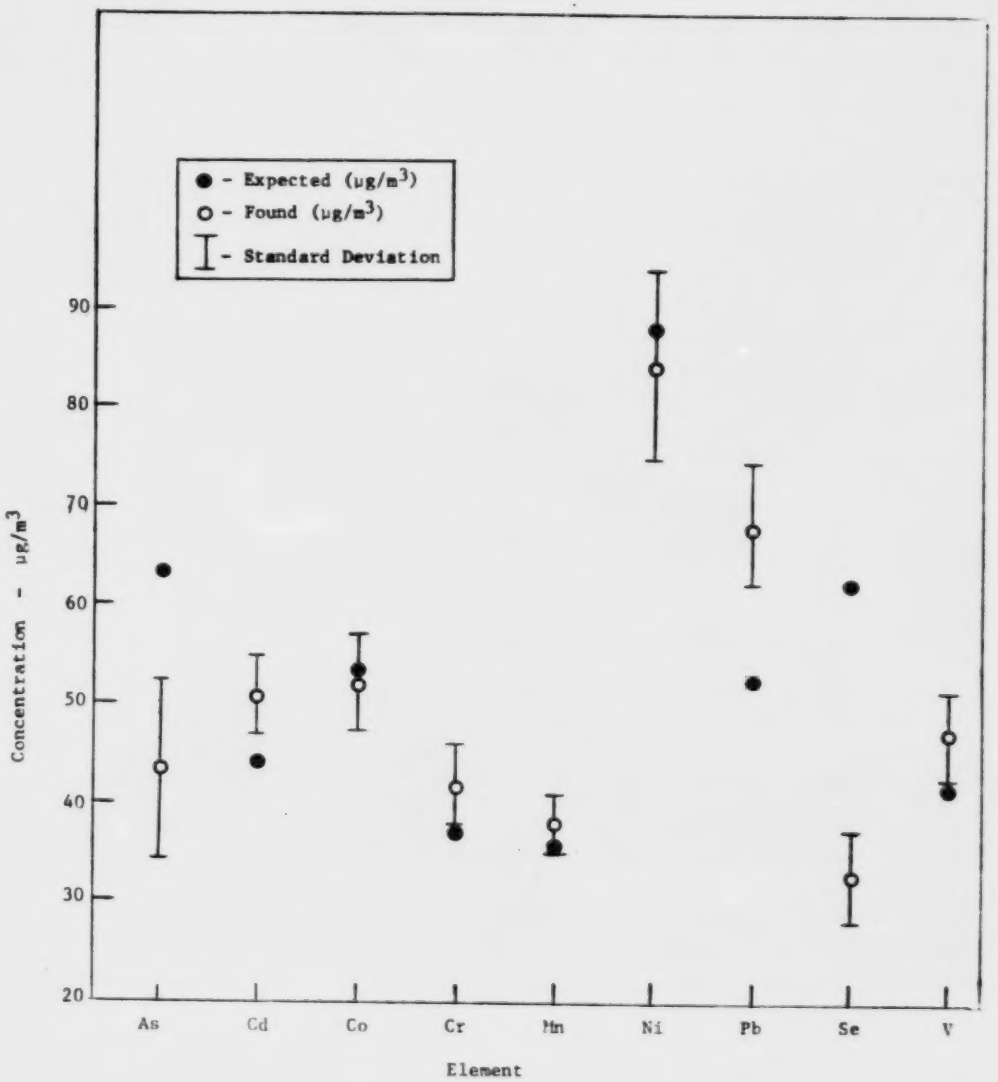

Figure 5. Graphical presentation of precision and accuracy.

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APPENDIX A

DESIGN OF SOURCE SIMULATION APPARATUS

To determine the suitability of the source simulation apparatus design, engineering calculations were carried out as follows:

1) Preliminary Design Basis

Fuel - No. 2 distillate
Fuel consumption - 1-2 ml/sec
Duct size - 20 cm diameter
Stack gas temperature - 150°C (300°F)
Dilution air temperature - 25°C (75°F)
Assume no heat loss to system
Suitable for isokinetic sampling with 1 cm (3/8") diameter nozzle

2) Engineering Calculations

Engineering computations were carried out as follows to determine the suitability of the source simulation unit design.

- Design Basis:

No. 2 fuel oil
1 ml/sec (1 gal/hr) fuel consumption
20 cm (8 inch) diameter duct
dilution air at 25°C (75°F)
no heat loss to system
stack gas temperature of 150°C (302°F)
0.94 cm (3/8 inches) diameter nozzle and isokinetic sampling

The following sample calculation was made for an indication of stack gas velocity, particulate loading, etc.

- Typical fuel composition (ultimate analysis)

C	85.6%	x	12	=	10.27
H	12.0		2		0.24
S	0.35		32		0.11
N	0.5		14		0.07
O	0.6		12		0.07
			M_{av}		10.76

- Combustion gas volume

			Equivalent Volumes			
			Fuel	Oxygen	Air	Total
$C \rightarrow CO_2$	85.6/12	=	7.13	14.26	67.9	75.03
$H \rightarrow H_2O$	12.0/2		6.00	3.0	14.3	20.30
$S \rightarrow SO_2$	0.35/32		0.01	0.02	0.1	0.11
N	0.05/14		0.04	--	--	0.04
O	0.06/16		0.04	(0.04)	(0.2)	(0.16)
			13.21		82.0	95.32

At 20% excess combustion air: $13.21 + 1.2(82.0) = 111.61$

Basis: 1 liter fuel

1 liter fuel = 896 g

$$896\ g \times \frac{1\ mole}{10.8\ g} \times \frac{24.47\ell}{mole} \times \frac{1\ m^3}{10^3\ell} = 1.98\ m^3$$

Stack gas volume: $\frac{111.61}{13.21} \times 1.98 = 16.76\ m^3$

- Gas Temperature

1 liter fuel = 9470 Cal. $\quad H = m\ C_p \Delta T$

$$\Delta T = 9470\ Cal \times \frac{1}{0.511\ Cal/g\text{-}°C} \times \frac{1}{1.293\ g/\ell} \times \frac{1\ m^3}{10^3\ell} \times \frac{10^3\ Cal}{1\ Cal} \times 16.76 \times \frac{1}{16.76\ m^3} = 855$$

For $T_{air} = 25°C$, $T_{combution\ gas} = 830°C$

- Dilution Air:

Let (1-x) represent the volume fraction of combustion gas in the stack stream.

$T_{stack\ gas} = 830\ (1-x) + 25x$

For $T_{stack\ gas} = 150°C$, $x = 0.845$

Dilution air = $108.13\ m^3$

Total stack gas = $124.9\ m^3$

- Stack gas velocity:

  For 20 cm (8 in) duct, area = 0.031 m^2 (0.35 ft^2)

  For fuel consumption of 1 ml/sec (1 gallon/hour),

  $$v_{\text{stack gas}} = 4.3 \text{ m/sec } (13.8 \text{ ft/sec})$$

- Isokinetic sampling rate:

  For 0.94 cm (3/8 in) nozzle, area sampled/area total = 0.0022

  Volume sampled - 0.0022 x 124.9 x 3.785 = 1.04 m^3

- Trace element concentration:

  For concentration of 100 $\mu g/m^3$,

  $\frac{104 \ \mu g}{0.0022}$ = 47.2 mg added to 3.785 liters (1 gallon) fuel

APPENDIX B

ANALYSIS RESULTS FOR INDIVIDUAL SAMPLES

The following tables present analytical results for the individual samples collected for each run and for the distribution of metals among these samples. The individual samples are identified as follows:

F1 - filter, extraction by 6N HNO_3.

F2 - filter, second extraction by 6N HNO_3.

AP - acetone-water probe wash.

WP - water probe wash.

NP1 - nitric acid probe wash (6N HNO_3, except as noted).

NP2 - record nitric acid probe wash (6N HNO_3, except as noted).

I1 - impinger solutions and rinse (6N HNO_3, except as noted).

I2 - record impinger rinse (6N HNO_3, except as noted).

RUN 2

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	Cu		Fe		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	--		--										--				--					
Found																						
F 1	6.5		20.2										1.3				62					
F 2																						
AP	0.3		9.0										0.9				0.5					
WP																						
NP 1	2.6		20.2										1.4				2					
NP 2																						
I 1	3.6		25.0										1.5				2					
I 2																						
Total	13.0		74.4										5.1				66.5					
Train B																						
Expected	--		--										--				--					
Found																						
F 1	8.5		10.2										1.2				59					
F 2																						
AP	0.5		8.1										0.4				0.5					
WP																						
NP 1	1.8		10.8										0.8				2					
NP 2																						
I 1	5.0		26.6										1.5				4					
I 2																						
Total	15.8		55.7										3.9				65.5					

RUN 3

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	Cu		Fe		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	--		--										--				--					
Found																						
F 1	4.3		15.9										0.83				43.5					
F 2																						
AP	0.3		4.0										0.45				1.0					
WP																						
NP 1	<0.3		10.0										0.2				3.0					
NP 2																						
I 1	2.0		12.8										1.3				1.2					
I 2																						
Total	6.9		49.7										2.8				48.7					
Train B																						
Expected	--		--										--				--					
Found																						
F 1	5.4		16.1										0.71				47.5					
F 2																						
AP	0.3		14.2										0.48				0.5					
WP																						
NP 1	<0.3		10.7										0.5				2.2					
NP 2																						
I 1	<0.3		70*										79.8*				3.5					
I 2																						
Total	6.3		>41.0										>1.7				53.7					
*Sample Contamination																						

RUN 4

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	Cu		Fe		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected													223(100)									
Found																						
F 1	4.4		9.5										152(68)				39.8					
F 2																						
AP	2.0		5.8										2.5(1)				0.5					
WP																						
NP 1	2.0		7.8										1.6(1)				<4					
NP 2																						
I 1	2.5		14.7										1.5(1)				<5					
I 2																						
Total	10.9		37.8										157.6(71)				49.3					
Train B																						
Expected													223(100)									
Found																						
F 1	5.3		7.2										143(64)				36.8					
F 2																						
AP	1.0		3.4										2.2(1)				<0.5					
WP																						
NP 1	0.3		9.9										2 (1)				<3					
NP 2																						
I 1	2.9		20.8										0.4 -				<3.6					
I 2																						
Total	9.5		41.3										147.6(66)				43.9					

RUN 5

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected																						
Found					1.6		0.6						0.5		1.0						4	
F 1																						
F 2					1.0		<0.1						0.5		.8						4	
AP																						
WP					<0.3		<0.3						<0.3		1.3						<3	
NP 1																						
NP 2					2		<0.5						<0.5		3.0						<5	
I 1																						
I 2					4.9		1.5						1.8		6.1						<16	
Total																						
Train B																						
Expected																						
Found					0.7		<0.2						0.7		3.0						<1	
F 1																						
F 2					0.9		<0.1						0.4		<0.1						<1	
AP																						
WP					<0.3		<0.3						<0.3		0.8						<3	
NP 1																						
NP 2					1.6		<0.5						1.0		3.1						<5	
I 1																						
I 2					3.5		1.1						2.4		7.0						<10	
Total																						

RUN 7

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected					194	(100)	334	(100)					205	(100)	276	(100)					211	(100)
Found					189	(97)	294	(88)					167	(81)	264	(96)					190	(90)
F 1																						
F 2					11.4	(6)	11.5	(3)					7.9	(4)	11.3	(4)					<0.5	-
AP																						
WP					6.2	(3)	9.5	(3)					5.7	(3)	5.2	(2)					<10	(5)
NP 1																						
NP 2					<1	(1)	<1	-					<1	-	2.5	(1)					<10	(5)
I 1																						
I 2																						
Total					207	(107)	316	(94)					182	(88)	283	(103)					211	(100)
Train B																						
Expected					200	(100)	344	(100)					211	(100)	285	(100)					218	(100)
Found					198	(99)	316	(92)					203	(96)	295	(104)					209	(96)
F 1																						
F 2					11.4	(6)	11.5	(3)					7.9	(4)	11.5	(4)					<0.5	-
AP																						
WP					4.7	(2)	6.1	(2)					4.7	(2)	2.8	(1)					<10	(5)
NP 1																						
NP 2					<1	-	<1	-					<1	-	1.6	(1)					<10	(5)
I 1																						
I 2																						
Total					214	(107)	334	(97)					217	(102)	310	(110)					230	(106)

RUN 8

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	--				--		--								--		--		--		--	
Found																						
F 1	<0.1				2		4.0								2.0		2.0		<0.2		4.0	
F 2	<0.1				<0.5		<0.7								0.2		<2.5		<0.2		2	
AP	<0.1				1		0.5								3.0		1.0		<0.2		2	
WP																						
NP 1	<0.5				<0.5		<0.5								0.5		<5		<0.5		<5	
NP 2																						
I 1	0.5				0.5		0.5								2		<5		1		5	
I 2																						
Total	1.3				4.5		6.2								5.7		15.5		2.1		18	
Train B																						
Expected																						
Found																						
F 1																						
F 2																						
AP																						
WP																						
NP 1																						
NP 2																						
I 1																						
I 2																						
Total																						

RUN 9

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected					185	(100)	183	(100)					183	(100)	192	(100)	203	(100)			218	(100)
Found																						
F 1					188	(102)	195	(107)					188	(103)	225	(117)	226	(111)			213	(98)
F 2					6	(3)	<3	(1)					6	(3)	9	(5)	15	(7)			10	(5)
AP					12	(6)	12	(6)					12	(7)	12	(6)	14	(7)			8	(4)
WP																						
NP 1					15	(9)	13	(6)					15	(8)	19	(10)	16	(8)			11	(5)
NP 2																						
I 1					1	-	<0.5	-					11	(6)	2	(1)	2	(1)			<3	(1)
I 2																						
Total					222	(120)	224	(120)					232	(127)	267	(139)	273	(134)			245	(113)
Train B																						
Expected																						
Found																						
F 1																						
F 2																						
AP																						
WP																						
NP 1																						
NP 2																						
I 1																						
I 2																						
Total																						

RUN 10

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected					183	(100	182	(100)					182	(100)	191	(100)	202	(100)			216	(100)
Found																						
F 1					187	(102)	190	(104)					192	(105)	190	(99)	225	(111)			197	(73)
F 2					3	(1)	3	(2)					3	(1)	4	(2)	3	(1)			<3	(1)
AP					11	(6)	14	(8)					14	(8)	14	(7)	15	(7)			11	(5)
WP																						
NP 1					13	(7)	12	(7)					12	(7)	13	(7)	15	(7)			9	(4)
NP 2																						
I 1					<0.5	-	<0.5	-					15	(8)	2	(1)	2	(1)			<3	(1)
I 2																						
Total					214	(116)	219	(121)					236	(129)	223	(116)	260	(127)			183	(84)
Train B																						
Expected																						
Found																						
F 1																						
F 2																						
AP																						
WP																						
NP 1																						
NP 2																						
I 1																						
I 2																						
Total																						

RUN 11

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	179	(100)							200	(100)			151	(100)					183	(100)		
Found																						
F 1	71	(40)							136	(68)			149	(99)					43	(33)		
F 2	4	(2)							10	(5)			8	(5)					2	(1)		
AP	7	(4)							27	(14)			7	(5)					23	(13)		
WP																						
NP 1	6	(3)							19	(10)			10	(7)					4	(2)		
NP 2																						
I 1	6	(3)							1	-			22	(19)					7	(4)		
I 2																						
Total	94	(52)							193	(97)			196	(131)					79	(53)		
Train B																						
Expected	184	(100)							205	(100)			155	(100)					188	(100)		
Found																						
F 1	47	(26)							55	(27)			157	(101)					44	(23)		
F 2	2	(1)							10	(5)			7	(5)					1			
AP	9	(5)							17	(8)			7	(5)					23	(12)		
WP																						
NP 1	8	(4)							17	(8)			8	(5)					3	(1)		
NP 2																						
I 1	6	(3)							1	-			17	(11)					5	(3)		
I 2																						
Total	712	(39)							99	(49)			196	(127)					76	(39)		

RUN 12

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	208	(100)							245	(100)			165	(100)					213	(100)		
Found																						
F 1	52	(25)							136	(56)			136	(82)					53	(25)		
F 2	3	(1)							11	(4)			8	(5)					2	(1)		
AP	7	(3)							16	(7)			7	(4)					30	(15)		
WP																						
NP 1	5	(2)							20	(8)			9	(5)					1	-		
NP 2																						
I 1	4	(2)							2	(1)			33	(20)					7	(3)		
I 2																						
Total	71	(33)							185	(76)			193	(116)					93	(44)		
Train B																						
Expected	193	(100)							227	(100)			153	(100)					197	(100)		
Found																						
F 1	81	(42)							146	(64)			146	(95)					61	(31)		
F 2	2	(1)							9	(4)			6	(4)					0.8	-		
AP	8	(4)							11	(5)			7	(5)					39	(20)		
WP																						
NP 1	3	(2)							13	(6)			7	(5)					<0.4	-		
NP 2																						
I 1	2	(1)							<1	-			22	(14)					5	(3)		
I 2																						
Total	96	(50)							180	(79)			188	(123)					106	(54)		

RUN 16

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	102	(100)			80	(100)	115	(100)	94	(100)			77	(100)	124	(100)	74	(100)	104	(100)	73	(100)
Found																						
F 1	6	(6)			86	(103)	118	(103)	69	(73)			80	(104)	103	(83)	84	(114)	18	(17)	53	(73)
F 2	0.5	-			2	(2)	4	(4)	3	(3)			3	(4)	4	(3)	1	(1)	1.4	(1)	<0.1	
AP	3	(3)			5	(6)	3	(3)	10	(11)			3	(4)	4	(3)	2	(3)	12	(12)	4	(5)
WP																						
NP 1	0.7	(1)			4	(5)	<0.7	(1)	2	(2)			2	(3)	7	(6)	0.7	(1)	0.3		<2	(3)
NP 2																						
I 1	9	(9)			<0.7	(1)	<1	(1)	196*	-			0.7	(1)	5	(4)	<1	(1)	20	(19)	<3	(4)
I 2																						
Total	19	(19)			98	(117)	127	(112)	>84	(89)			89	(116)	123	(99)	89	(120)	52	(49)	62	(85)
Train B																						
Expected	105				82		118		97				79		127		76		106		77	
Found																						
F 1	6	(6)			82	(100)	99	(84)	65	(67)			75	(95)	74	(58)	81	(107)	19	(18)	55	(71)
F 2	1	(1)			3	(4)	4	(3)	3	(3)			3	(4)	3	(2)	0.6	(1)	<0.1		<0.1	-
AP	1	(1)			7	(9)	3	(3)	11	(11)			6	(8)	24	(19)	2	(3)	6	(6)	5	(7)
WP																						
NP 1	3	(3)			<0.6	(1)	<0.6	(1)	43	(44)			0.3	-	5	(4)	<0.6	(1)	<0.6	(1)	<2	(3)
NP 2																						
I 1	7	(7)			<0.6	(1)	<1	(1)	<0.6	(1)			1.0	(1)	3	(2)	8	(11)	18	(17)	<3	(4)
I 2																						
Total	18	(18)			94	(115)	108	(92)	123	(126)			85	(108)	109	(85)	93	(123)	44	(42)	65	(85)
*Sample Contamination																						

RUN 18

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	78	(100)					86	(100)					64	(100)	78	(100)	71	(100)	78	(100)	49	(100)
Found																						
F 1	15	(19)					46	(53)					42	(66)	43	(55)	58	(82)	9	(12)	40	(82)
F 2																						
AP	3	(4)					3	(3)					7	(11)	3	(4)	3	(4)	10	(13)	<2	(4)
WP (H_2O)	<0.2	-					1	(1)					8	(13)	1	(1)	1	(1)	<0.2	-	<2	(4)
NP 1	<0.2	-					<0.8	(1)					<0.5	(1)	<0.8	(1)	<1	(1)	<0.2	-	<2	(4)
NP 2																						
I 1 (H_2O)	<0.2	-					<0.8	(1)					1	(2)	<0.8	(1)	4	(6)	0.3	-	<2	(4)
I 2	<0.3	-					<0.5	(1)					<0.3	-	<0.5	(1)	1	(1)	<0.5	(1)	<0.3	(1)
Total	19	(23)					53	(60)					59	(92)	50	(64)	68	(96)	20	(26)	48	(98)
Train B																						
Expected	76	(100)					85	(100)					63	(100)	76	(100)	70	(100)	77	(100)	58	(100)
Found																						
F 1	28	(37)					57	(67)					67	(106)	57	(75)	90	(129)	18	(23)	50	(86)
F 2																						
AP	4	(5)					10	(12)					12	(19)	10	(13)	6	(9)	13	(17)	5	(9)
WP																						
NP 1	1	(1)					<0.8	(1)					<0.5	(1)	<0.8	(1)	3	(4)	0.3	-	2	(3)
NP 2	1	(1)					12	(14)					12	(19)	12	(16)	14	(20)	<0.2	-	<2	(3)
I 1	4	(5)					-	-					1	(2)	-	-	4	(1)	4	(5)	2	(3)
I 2																						
Total	38	(50)					80	(94)					92	(146)	80	(105)	117	(167)	35	(45)	61	(105)

RUN 19

AMOUNT (µg) AND PERCENT (%) METAL RECOVERED

Sample	As		Be		Cd		Co		Cr		Hg		Mn		Ni		Pb		Se		V	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Train A																						
Expected	92(100)						77(100)						76(100)		105(100)		84(100)		93(100)		70(100)	
Found																						
F 1	38 (41)						65 (84)						81(107)		75 (71)		86(102)		12 (13)		52 (74)	
F 2																						
AP	7 (8)						9 (12)						5 (7)		13 (12)		7 (8)		12 (13)		12 (17)	
WP																						
NP 1(0.1N HNO_3)	1 (1)						<0.5 (1)						0.6 (1)		<0.5 -		2 (2)		<0.6 (1)		2 (3)	
NP	- -						<0.5 (1)						0.5 (1)		0.5 -		1 (1)		<0.5 (1)		<0.5 (1)	
I 1(0.1N HNO_3)	4.5 (5)						<0.5 (1)						1 (1)		<0.5 -		2 (2)		<1 (1)		<0.5 (1)	
I 2	-						<0.7 (1)						1 (1)		2.5 (2)		2 (2)		<0.5 (1)		<0.5 (1)	
Total	51 (55)						76 (99)						89(117)		92 (88)		100(119)		26 (28)		67 (96)	
Train B																						
Expected	90(100)						75(100)						74(100)		103(100)		82(100)		91(100)		69(100)	
Found																						
F 1	39 (43)						66 (88)						78(105)		76 (74)		93(113)		15 (16)		58 (84)	
F 2																						
AP	5 (6)						4 (5)						6 (8)		9 (9)		5 (6)		8 (9)		9 (13)	
WP																						
NP 1	- -						1 (1)						2 (3)		5 (6)		4 (5)		4 (4)		7 (10)	
NP 2	- -						<0.6 (1)						<0.5 (1)		3 (3)		<0.1 -		<0.5 (1)		<0.5 (1)	
I 1	- -						<0.6 (1)						2 (3)		2 (2)		3 (4)		5 (5)		<0.5 (1)	
I 2																						
Total	>44 (49)						73 (97)						88(119)		96 (93)		105(128)		32 (35)		74(107)	

APPENDIX C

RECOMMENDED METHOD

RECOMMENDED METHOD FOR THE DETERMINATION OF CADMIUM, CHROMIUM, COBALT, MANGANESE, NICKEL, LEAD AND VANADIUM EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle - Stack emissions are isokinetically sampled from the source. Particulate is collected on a quartz fiber filter and metal-containing gases are collected in 0.1M nitric acid impinger solutions. The filter is extracted with nitric acid which is combined with the impinger and train rinse solutions. After acid digestion and reduction in volume, aliquot samples are analysed for specific metals by atomic absorption spectroscopy.

1.2 Applicability - The method is applicable for the determination of cadmium, cobalt, chromium, manganese, nickel, lead and vanadium emissions from stationary sources.

2. Apparatus

2.1 Sampling train - A schematic of the sampling train used by EPA is shown in Figure 1. Commercial models of this train are available, although construction details are described in APTD-0581,[1] and operating and maintenance procedures are described in APTD-0576. The components essential to this sampling train are the following:

2.1.1 Nozzle - Stainless steel or glass with sharp, tapered leading edge.

2.1.2 Probe - Sheathed borosilicate glass. A heating system capable of maintaining a minimum gas temperature in the range of the stack temperature at the probe outlet during sampling may be used to prevent condensation from occurring.

2.1.3 Pitot tube - Type S (Figure 2), or equivalent, with a coefficient within 5 percent over the working range, attached to probe to monitor stack gas velocity.

2.1.4 Differential pressure gauge - Inclined manometer, or equivalent, to measure velocity head to within 10 percent of the minimum value.

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[1] These documents are available for a nominal cost from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va. 22151.

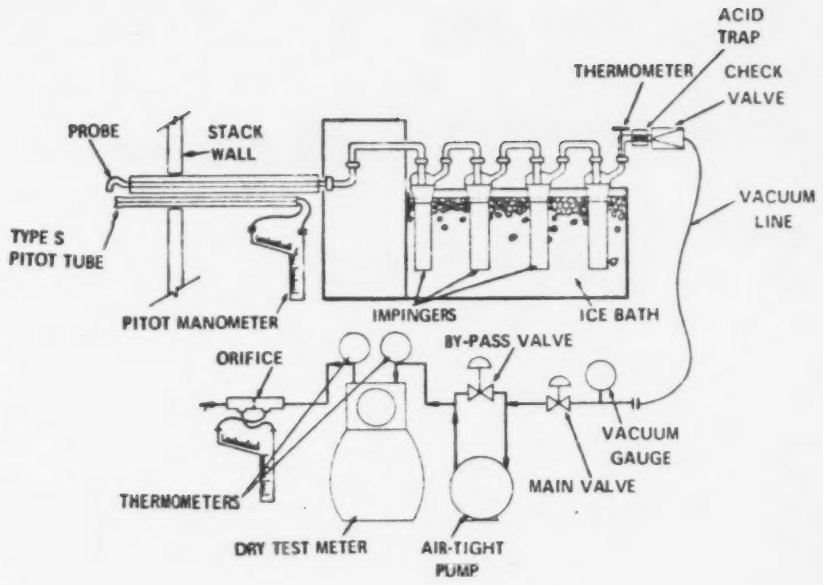


Figure 1. Sampling train.

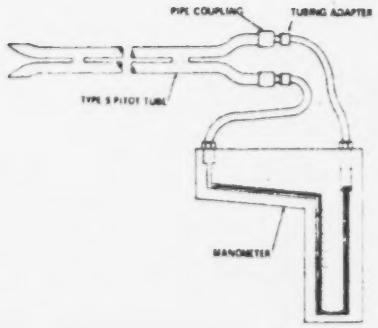


Figure 2. Pilot tube-manometer assembly.

2.1.5 Filter holder - Borosilicate glass. The filter holder must provide a positive seal against leakage from outside or around the filter. A heating system capable of maintaining the filter at a minimum temperature in the range of the stack temperature may be used to prevent condensation from occurring.

2.1.6 Impingers - Four Greenburg-Smith impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers may be modified by replacing the tip with a 1/2 inch i.d. glass tube extending to one-half inch from the bottom of the flask.

2.1.7 Metering system - Vacuum gauge, leakless pump, thermometers capable of measuring temperature to within 3°C dry gas meter with 2 percent accuracy, and related equipment, described in APTD-0581, to maintain an isokinetic sampling rate and to determine sample volume.

2.1.8 Barometer - To measure atmospheric pressure to within 2.5 mm Hg.

2.1.9 Measurement of stack conditions (stack pressure, temperature, moisture and velocity) - Pitot tube - Type S, or equivalent, with a coefficient within 5 percent over the working range.

2.1.10 Temperature gage - Any temperature measuring device to measure stack temperature to within 3°C.

2.1.11 Pressure gage - Pitot tube and inclined manometer or equivalent, to measure stack pressure to within 2.5 mm Hg.

2.1.12 Moisture determination - Wet and dry bulb thermometers, drying tubes, condensers, or equivalent, to determine stack moisture content to within 1 percent.

2.2 Sample Recovery

2.2.1 Probe and nozzle brushes - Nylon bristles with stainless steel wire handles. The probe brush shall have extensions of stainless steel, nylon, teflon or similarly inert materials. Both brushes shall be properly sized and shaped to brush out probe liner and nozzle.

2.2.2 Leakless sample bottles - 500 ml capacity.

2.2.3 Graduated cylinders - 250 and 500 ml capacity.

2.2.4 Funnel - Glass, long stem.

2.2.5 Wash bottles - 4 nalgene 500 ml capacity or equivalent.

2.2.6 Petri dish - Glass or polystyrene.

2.3 Analysis

2.3.1 Atomic absorption spectrophotometer - Perkin-Elmer Model 303, or instrument of equivalent sensitivity, equipped with burners for air/acetylene and N_2O/acetylene flames.

2.3.2 Hollow-cathode source lamps for cadmium, cobalt, chromium, manganese, nickel, lead and vanadium to fit spectrophotometer (2.3.1).

2.3.3 Autylene, air and nitrous oxide (N_2O) supplies for spectrophotometer (2.3.1).

2.3.4 Hot plate

2.3.5 Beakers, 50 ml, 150 ml and 600 ml with watch glass covers.

2.3.6 Volumetric flasks, 50 ml, 10 ml.

2.3.7 Centrifuge, 3200 rpm max. and 15 ml conical tubes.

2.3.8 Apparatus for cutting filters - either scissors with blades of polymeric (non-metallic) composition, or two spatulas having polymer-coated blades.

3.1 Stock Reagents

3.1.1 Water-distilled and deionized.

3.1.2 Nitric acid - Concentrated A.C.S. reagent grade, or equivalent.

3.1.3 Wash acid - 1/1 (V/V) nitric acid - distilled water.

3.1.4 Aluminum nitrate, reagent grade.

3.1.5 Standard solutions of cadmium, cobalt, chromium, manganese, nickel, lead and vanadium, each containing 1000 micrograms of element/ml, for calibration of atomic absorption spectrophotometer. Commercially prepared standard solutions should be checked against appropriate high purity metal or salt.

3.2 Sampling Reagents

3.2.1 Filter - Gelman Microquartz, or equivalent, high efficiency fiber filter exhibiting at least 99.95 percent efficiency on 0.3 micron dioctyl phthalate smoke particles. Filter material should have low background levels of trace metals.

3.2.2 Silica gel - Indicating type 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

3.2.3 Distilled and deionized water.

3.2.4 0.1M Nitric acid - Pipet 13 mls of concentrated nitric acid into two liter volumetric flask and bring to volume with distilled, deionized water. Allow to cool and transfer to pre-cleaned (see section 4.5.1) glass or polyethylene container.

3.2.5 6.0M Nitric acid - Add 500 mls of distilled, deionized water to 1 liter volumetric flask. Slowly add 385 mls of concentrated nitric acid to flask with stirring and cool to room temperature. Bring to final volume with distilled, deionized water.

3.2.6 Crushed ice.

3.2.7 Stopcock grease - Acetone insoluble, heat stable silicon grease. This is not necessary if screw-on connectors with teflon sleeves, or similar, are used.

3.3. Sample Recovery Reagents

3.3.1 Distilled and deionized water.

3.3.2 Acetone - Reagent grade.

3.3.3 0.1M Nitric acid.

3.3.4 6.0M Nitric acid.

3.4 Analysis Reagents

3.4.1 Distilled and deionized water.

3.4.2 Nitric acid, concentrated reagent grade.

3.4.3 Nitric acid, 1 molar, dilute 61 ml of concentrated nitric acid (3.4.2) with water (3.4.1) to 1 liter.

3.4.4 Aluminum nitrate solution, 10 milligram Al/ml, dissolve 13.9 g $Al(NO_3)_2 \cdot 9\ H_2O$ in water (3.4.1) and dilute to 100 ml.

3.5 Standard Solutions

3.5.1 Standard solutions of cadmium, cobalt, chromium, manganese, nickel, lead and vanadium for calibration of spectrophotometer. Prepare from the stock standard solutions (3.1.5) by dilution to calibration range in table below using 1 molar nitric acid (3.4.3) except for vanadium to which aluminum nitrate solution (3.4.4) is also added to yield an aluminum concentration of 1 milligram/ml in the final solution.

Element	Calibration Range (µg/ml)
cadmium	0.02 to 2
chromium	0.1 to 3
cobalt	0.2 to 5
manganese	0.05 to 3
nickel	0.2 to 5
lead	0.05 to 5
vanadium	0.5 to 10

These dilute standard solutions should be prepared fresh daily.

4. Procedure

4.1 Guidelines for source testing are detailed in the following sections. These guidelines are generally applicable; however, most sample sites differ to some degree and temporary alterations such as stack extensions or expansions often are required to insure the best possible sample site. Further, since the metals for which this method applies may be hazardous, care should be taken to minimize exposure. Finally, since the total quantity of metals to be collected is quite small, the test must be carefully conducted to prevent contamination or loss of sample.

4.2 Selection of a sampling site and minimum number of traverse points.

4.2.1 Select a suitable sampling site that is as close as practicable to the point of atmospheric emission. If possible, stacks smaller than 0.3 m (1 ft) in diameter should not be sampled.

4.2.2 The sampling site should be at least 8 stack or duct diameters downstream and 2 diameters upstream from any flow disturbance such as a bend, expansion or contraction. For a rectangular cross-section, determine an equivalent diameter from the following equation:

$$D_e = \frac{2LW}{L+W}$$

where:

D_e = equivalent diameter

L = length

W = width

4.2.3 When the above sampling site criteria can be met, the minimum number of traverse points is four (4) for stacks 0.3 m (1 ft) in diameter or less, eight (8) for stacks larger than 0.3 m (1 ft) but 0.6 m (2 ft) in diameter or less, and twelve (12) for stacks larger than 0.6 m (2 ft).

4.2.4 Some sampling situations may render the above sampling site criteria impractical. When this is the case, choose a convenient sampling location and use Figure 3 to determine the minimum number of traverse points. However, use Figure 3 only for stacks 0.3 m (1 ft) in diameter or larger.

4.2.5 To use Figure 3, first measure the distance from the chosen sampling location to the nearest upstream and downstream disturbances. Divide this distance by the diameter, or equivalent diameter, to determine the distance in terms of pipe diameters. Determing the corresponding number of traverse points for each distance from Figure 3. Select the higher of the two numbers of traverse points, or a greater value, such that for circular stacks the number is a multiple of four, and for rectangular stacks the number follows the criteria of section 4.3.2.

4.2.6 If a selected sampling point is closer than 2.5 cm (1 in) from the stack wall, adjust the location of that point to ensure that the sample is taken at least 2.5 cm (1 in) away from the wall.

4.3 Cross-sectional layout and location of traverse points.

4.3.1 For circular stacks, locate the traverse points on at least two diameters according to Figure 4 and Table 1. The traverse axes shall divide the stack cross section into equal parts.

4.3.2 For rectangular stacks, divide the cross section into as many equal rectangular areas as traverse points, such that the ratio of the length to the width of the elemental areas is between 1 and 2. Locate the traverse points at the centroid of each equal area according to Figure 5.

4.4 Measurement of stack conditions.

4.4.1 Set up the apparatus as shown in Figure 2. Make sure all connections are tight and leak free. Measure the velocity head and temperature at the traverse points specified by sections 4.2 and 4.3.

4.4.2 Measure the static pressure in the stack.

4.4.3 Determine the stack gas moisture.

4.4.4 Determine the stack gas molecular weight from the measured moisture content and knowledge of the expected gas stream composition. A standard Orsat analyzer has been found valuable at combustion sources. In all cases, sound engineering judgment should be used.

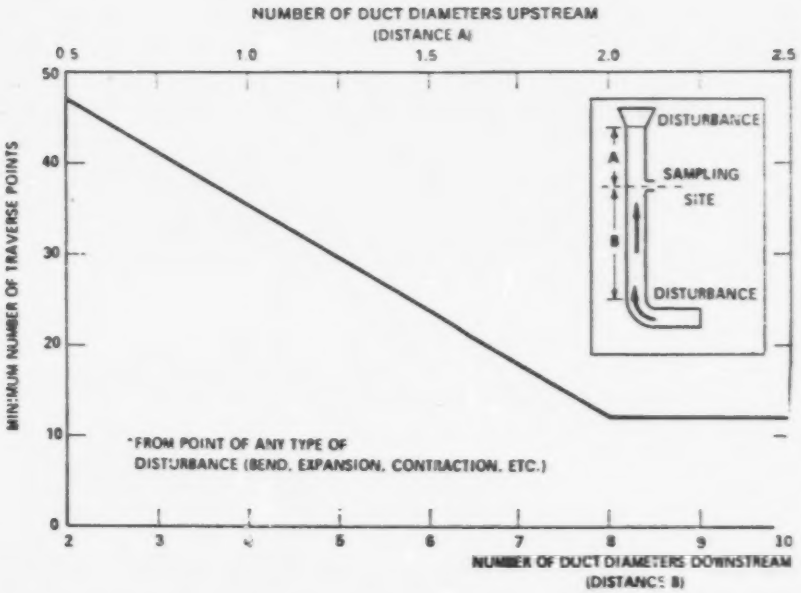


Figure 3. Minimum number of traverse points.

Figure 4. Cross section of circular stack showing location of traverse points on perpendicular diameters.

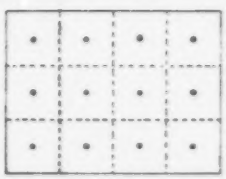


Figure 5. Cross section of rectangular stack divided into 12 equal areas with traverse points at centroid of each area.

TABLE 1. LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS (PERCENT OF STACK DIAMETER FROM INSIDE WALL TO TRAVERSE POINT.)

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

4.5 Pre-sampling operations.

4.5.1 Prior to assembly, clean all train glassware (impingers, filter holder and glass connectors) by washing in a soap and water bath, soaking for two hours in wash acid, rinsing with acetone and then 3 times with distilled deionized water. The probe liner may be cleaned by plugging one end with a rubber stopper, and half filling the column with soap and water. Vigorously brush the entire length using a brush and then drain and flush with water. Re-insert rubber stopper and fill liner with wash acid. Allow to stand for two hours before draining. Rinse liner with acetone and then 3 times with distilled, deionized water. Place 100 mls of 0.1M nitric acid in each of the first two impingers, leave the third impinger empty, and place approximately 200 gm of preweighed silica gel in the fourth impinger. Save a portion of the 0.1M nitric acid as a blank in the sample analysis. Set up the train and the probe as in Figure 1.

4.5.2 Leak check the sampling train at the sampling site. The leakage rate should not be in excess of 1 percent of the desired sampling rate, .0006 m^3/min (0.2 cfm). If condensation in the probe or filter is a problem, probe and filter heaters will be required. Adjust the heaters to provide a temperature of 120 $\pm$ 14°C (248 $\pm$ 25°F). Place crushed ice around the impingers. Add more ice during the test to keep the temperature of the gases leaving the last impinger at 20°C (68°F).

4.6 Train operation.

4.6.1 For each run, record the data required on the example sheet shown in Figure 6. Take readings at each sampling point at least every 5 minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate.

4.6.2 Sample at a rate of 0.014-0.028 m^3/min (0.5 to 1.0 ft^3/min). Samples shall be taken over such a period or periods as are necessary to accurately determine the maximum emissions which would occur in a 24-hour period. In the case of cyclic operations, sufficient tests shall be made so as to allow accurate determination or calculation of the emissions which will occur over the duration of the cycle. A minimum sample time of 2 hours is recommended.

4.6.3 To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs which aid in the rapid adjustment of the sampling rate without other computations are in APTD-0576 and are available from commercial suppliers. Note that standard monographs are applicable only for type S pitot tubes and air or a stack gas with an equivalent density. Contact EPA or the sampling train supplier for instructions when the standard monograph is not applicable.

PLANT_____
LOCATION_____
OPERATOR_____
DATE_____
RUN NO._____
SAMPLE BOX NO._____
METER BOX NO._____
METER $\Delta H_@$_____
C FACTOR_____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE_____
BAROMETRIC PRESSURE_____
ASSUMED MOISTURE,%_____
HEATER BOX SETTING_____
PROBE LENGTH, m_____
NOZZLE DIAMETER, (CM)_____
PROBE HEATER SETTING_____

TRAVERSE POINT NUMBER	SAMPLING TIME MIN.	STATIC PRESSURE (P_S), mmHg	STACK TEMPERATURE (T_S), °C	VELOCITY HEAD (ΔP_S) mmH_2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH) mmH_2O	GAS SAMPLE VOLUME (Vm), m^3	GAS SAMPLE TEMPERATURE AT DRY GAS METER INLET (Tm_{In})°C	OUT (Tm_{Out})°C	SAMPLE BOX TEMPERATURE °C	IMPINGER TEMPERATURE °C	PROBE TEMPERATURE °C
TOTAL							Avg.	Avg.			
AVERAGE							Avg.				

Figure 6. Field data.

4.6.4 Turn off the pump at the conclusion of each run and record the final readings. Immediately remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in section 4.7.

4.7 Sample recovery.

4.7.1 (All storage bottles and the graduated cylinder must be precleaned as in section 4.5.1.) This operation should be performed in an area free of possible metal contamination. When the sampling train is moved, care must be exercised to prevent breakage and contamination.

4.7.2 Disconnect the probe from the impinger train. Remove the filter and any loose particulate matter from the filter holder and place in a petri dish. Place the contents (measured to $\pm$ 1 ml) of the first three impingers into another sample bottle. Rinse the probe and all glassware between it and the back half of the third impinger with 0.1M nitric acid, measuring the volume and add this to the latter sample bottle. Repeat impinger train glassware washing 3 additional times with 6.0M nitric acid, measure volume and retain for analysis. Clean the probe and nozzle by brushing, together with adding intermittent volumes of acetone and distilled water, collecting the wash solutions in a sample bottle. Disconnect the nozzle from the probe, and rewash the button hook nozzle with acetone and water with brushing. Rinse the bristles of the brushes with acetone/water and collect as above. Retain a sample of the acetone and water as blanks. Partially fill one sample bottle with approximately 200 mls of 0.1M nitric acid. Place an empty sample bottle under the blunt end of the probe. Insert glass funnel into probe liner and carefully pour nitric acid through probe while rotating to wet all inner probe surfaces. After the nitric acid has drained from the probe, switch sample bottles and repeat sequence two additional times. Seal and label sample bottle. Transfer approximately 200 mls of 6.0M nitric acid into previously used empty sample bottle. Place an empty bottle under tip of probe, and carefully pour contents of first through funnel and probe while revolving, into second bottle. Switch containers and repeat two additional times. Rinse probe liner, funnel and empty sample bottle three times with fresh 6.0M nitric acid and recover. Rinse all acid wetted surfaces with distilled, deionized water and discard washings. Retain blanks of both the 0.1M and 6.0M nitric acid. The inner surfaces of the front half of the filter holder and the cyclone bypass on cyclone should be washed with each solution used above and added to the appropriate sample bottles (three washes; acetone/water, 0.1M nitric acid and 6.0M nitric acid). Place the silica gel into a plastic jar and seal. Seal and secure each of the six sample containers and four reagent blank containers for shipment. If additional tests are desired, freshly cleaned glassware (described in section 4.5.1) must be used.

4.8 Analysis

4.8.1 Apparatus preparation - Clean all analysis glassware and filter-cutting equipment thoroughly with laboratory glassware detergent,

rinse with water, soak in wash acid (3.1.3) for 2-3 minutes and rinse thoroughly with distilled water (3.3.1). Adjust spectrophotometer, according to the instrument manual, for the flame and wavelength settings given for the metal(s) to be measured.

4.8.2 Sample preparation - The samples are digested with nitric acid.

4.8.2.1 Cut or tear the filter into small (3 cm x 3 cm) pieces, using either the plastic scissors or two plastic-coated spatulas (2.3.8). Transfer the filter pieces and any loose particulate matter from the sample container into a 150 ml beaker. Add 50 ml of concentrated nitric acid, cover with watch glass, and heat on hot plate at below boil for two hours.

4.8.2.2 Transfer portions of the acetone-water probe wash to a 150 ml beaker and evaporate on hot plate adding remainder of acetone-water solution until all solution has been transferred. When volume reaches approximately 10 ml, add 10 ml of concentrated nitric acid and continue evaporation down to 10 ml.

4.8.2.3 Evaporate combined nitric acid probe washes and impinger solutions in a 600 ml beaker down to a volume of approximately 50 ml.

4.8.2.4 Decant the filter extract (4.8.2.1) into the acetone-water probe wash beaker (4.8.2.2) while minimizing the amount of solids transferred. Wash the filter solids two times with distilled water and transfer these washings into the acetone-water probe wash beaker. Evaporate down to approximately 25 ml.

4.8.2.5 Transfer the solutions from both 4.8.2.3 and 4.8.2.4 into a 50 ml beaker while evaporating to a final volume of 2-3 ml. Dilute to 50 ml with distilled water (3.3.1).

4.8.2.6 Pipet a 10 ml aliquot of 4.8.2.5 into a 50 ml beaker, add 1 ml of aluminum nitrate solution (3.4.4), evaporate to approximately 4 to 5 ml and dilute to 10 ml with distilled water (3.3.1).

4.8.2.7 Weigh the spent silica gel and record to the nearest gram.

4.8.3 Measurement of metals - The sample solutions prepared in 4.8.2.5 and 4.8.2.6 are analyzed for the metals of interest by means of atomic absorption spectrophotometry. The instrument conditions for each element are given in Table 2. Calibration solutions are given in 3.5.1. If apparent sample concentrations exceed the calibration limits, the sample solutions should be diluted with 1 molar nitric acid, including aluminum for vanadium measurements.

TABLE 2. AA SPECTROPHOTOMETER SETTINGS

Metal	Wavelength (nm)	Flame
cadmium	228.8	air/acetylene
chromium	357.9	air/acetylene-reducing
cobalt	240.7	air/acetylene
manganese	279.5	air/acetylene
nickel	232.0	air/acetylene
lead	283.3	air/acetylene
vanadium	318.3	N_2O/acetylene-reducing

The results are to be expressed as concentrations (µg/ml) of metals in the measured solutions.

4.8.4 Analysis of reagent and filter blanks - The complete analysis workup and measurement scheme should be carried out on at least one filter from the same lot as that used in the sampling train, as well as on equivalent quantities of the same lots of reagents. The results are expressed as concentrations (μg/ml) of metals in the measured solutions.

5. Calibration

5.1 Sampling train.

5.1.1 Use standard methods and equipment as detailed in APTD-0576 to calibrate the rate meter, pitot tube, dry gas meter and probe heater (if used). Recalibrate prior to each test series.

5.2 Analysis.

5.2.1 Standardization is made with the procedure as suggested by the manufacturer with standard solutions prepared as described in 3.5.1. The linearity of working range should be established with a series of standard solutions. If collected samples are out of the linear range, the samples should be diluted. Standards should be interspersed with the samples since the calibration can change slightly with time.

6. Calculations

6.1 Average dry gas meter temperature, stack temperature, stack pressure and average orifice pressure drop. See data sheet (Figure 6).

6.2 Dry gas volume - Correct the sample volume measured by the dry gas meter to standard conditions (20°C and 760 mm Hg or 68°F and 29.92 in Hg) by using equation 1.

$$V_{M\ (STD)} = V_M \left(\frac{T_{STD}}{T_M} \right) \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{STD}} \right) \qquad \text{Eq. 1}$$

where:

$V_{M\ (STD)}$ = Volume of gas sampled through gas meter corrected to standard conditions (m^3, ft^3).

V_M = Volume of gas sampled through gas meter at meter conditions (m^3, ft^3).

$T_{(STD)}$ = Standard absolute temperature (293°K or 528°R).

T_M = Absolute average dry gas meter temperature (°K, °R).

P_{bar} = Barometric pressure at the sampling point (mm Hg, in Hg).

ΔH = Average pressure drop across the orifice meter (mm H_2O, in H_2O).

13.6 = Specific gravity of mercury.

P_{STD} = Standard absolute pressure (760 mm Hg, 29.92 in Hg).

6.3 Volume of water vapor at standard conditions.

$$V_{W\ (STD)} = \frac{V_{WC} \times R \times T_{STD}}{18\ (P_{STD})} \qquad \text{Eq. 2}$$

where:

$V_{W\ (STD)}$ = Volume of water vapor within sampled gas (m^3, ft^3) corrected to standard conditions.

V_{WC} = Total volume of water collected in impingers and silica gel (ml); see Figure 7 for conversion.

R = Ideal gas law constant (0.06236 mm Hg - m^3/K-gm mole) or (0.04813 in Hg - ft^3/°R-lb mole).

$T_{(STD)}$ = Absolute standard temperature (293°K, 528°R).

18 = Molecular weight of water (gm-/gm mole, lb-/lb mole).

$P_{(STD)}$ = Standard absolute pressure (760 mm Hg, 29.92 in Hg).

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* ml

*CONVERT WEIGHT OF WATER TO VOLUME BY dividing total weight increase BY DENSITY OF WATER. (1 g/ml):

$$\frac{\text{INCREASE, g}}{(1\ \text{g/ml})} = \text{VOLUME WATER, ml}$$

Figure 7. Analytical data.

6.4 Moisture content (percentage volume).

$$B_{W(STD)} = \frac{V_{W(STD)}}{V_{M(STD)} + V_{W(STD)}} \times 100 \qquad \text{Eq. 3}$$

where:

$B_{W(STD)}$ = Water vapor in the gas stream, percentage by volume.

$V_{W(STD)}$ = Volume of water vapor collected at standard conditions (m^3, ft^3).

$V_{M(STD)}$ = Volume of dry gas collected at standard conditions (m^3, ft^3).

100 = Conversion to percent.

6.5 Total gas volume sampled at standard conditions.

$$V_{TOT(STD)} = V_{W(STD)} + V_{M(STD)} \qquad \text{Eq. 4}$$

where:

$V_{TOT(STD)}$ = Total volume of gas sampled at standard conditions (m^3, ft^3).

$V_{W(STD)}$ = As above.

$V_{M(STD)}$ = As above.

6.6 Stack gas velocity at stack conditions.

Figure 8 shows a sample recording sheet for velocity traverse data. Use the averages in the last two columns of Figure 8 to determine the average stack gas velocity from Equation 5.

$$(V_S)_{avg} = K_P\, C_P\, (\sqrt{\Delta p})_{avg} \sqrt{\frac{(T_S)_{avg}}{P_S\, M_S}} \qquad \text{Eq. 5}$$

where:

$(V_S)_{avg}$ = Average stack gas velocity (m/sec, ft/sec)

K_P = Constant $\left(85.53\ {}^{ft}/_{sec} \left(\frac{\text{lb-in Hg}}{\text{lb mole-}^\circ\text{R-in } H_2O}\right)^{1/2}\right)$

PLANT_____

DATE _____

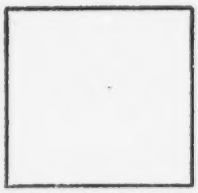
RUN NO._____

STACK DIAMETER (CM)_____

BAROMETRIC PRESSURE (mmHg)_____

STATIC PRESSURE IN STACK (P_g), (mmHg)_____

OPERATORS_____



SCHEMATIC OF STACK CROSS SECTION

Traverse Point Number	Velocity Head, (mm H_2O)	$\sqrt{\Delta_P}$	Stack Temperature (T_S), °C
	AVERAGE:		

Figure 8. Velocity traverse data.

C_P = Pitot coefficient, dimensionless.

$\sqrt{\Delta P}_{avg}$ = Average square root of the velocity head of stack gas (mm H_2O, in $H_2O)^{1/2}$

$(T_S)_{avg}$ = Average stack gas temperature (°K, °R).

P_S = Stack pressure, $P_{bar} \pm$ static pressure (mm Hg, in Hg).

M_S = Molecular weight of stack gas (wet basis) (gm/gm mole, lb/lb mole).

6.7 Average sampling velocity at stack conditions

$$(V_{sam}) = V_{T(STD)} \times \frac{T_{STD}}{T_{STK}} \times \frac{P_{STK}}{P_{STD}} \times \frac{4C^2}{\Pi(D^2)} \times \frac{1}{t} \qquad \text{Eq. 6}$$

where:

V_{sam} = Velocity of sampled gas through nozzle at stack conditions (m/sec, ft/sec).

$V_{T(STD)}$ = Total volume sampled at standard conditions (m^3, ft^3).

$T_{(STD)}$ = Absolute standard temperature (293°K, 528°R).

T_{STK} = Absolute stack temperature (°K, °R).

P_{STK} = Stack pressure $P_{bar} \pm$ static pressure (mm Hg, in Hg).

P_{STD} = Absolute pressure (760 mm Hg, 29.92 in Hg).

Π = pl , 3.141

D = Nozzle diameter (cm, in).

c = Conversion factor (144 in^2/ft^2 , 10000 cm^2/m^2).

t = Time (sec).

6.8 Isokineticity

$$I = \frac{(V_{sam})}{(V_S)} \times 100 \qquad \text{Eq. 7}$$

where:

I = Percent isokineticity.

(V_{sam}) = As above.

(V_S) = As above.

6.9 Amount(s) of metal(s) collected - calculate the total weight of metal collected, as follows.

$$W_m = 50\ (C_m\ D - C_B) \qquad \text{Eq. 8}$$

where:

W_m = Total weight of metal collected.

50 = Volume (ml) of measured solution.

C_m = Measured concentration (µg/ml) of metals in sample solution.

C_B = Measured concentration (µg/ml) of metals in filter and reagent blank solution.

D = Dilution factor for any dilutions required in sample measurement, expressed as $\left(\frac{\text{diluted volume}}{\text{aliquot taken}}\right)$.

6.10 Metal concentration in gas sample.

$$C_m = \frac{W_m}{V_{T(STD)}} \qquad \text{Eq. 9}$$

where:

C_m = Concentration of specific metal species (µg/m^3).

W_m = Weight of metal found by analysis µg.

$V_{T(STD)}$ = Total volume of gas sampled corrected to standard conditions (760 mm Hg, 20°C) (m^3).

7. Evaluation of Results

7.1 Determination of compliance.

7.1.1 Each performance test shall consist of three repetitions of the applicable test method. For the purpose of determining compliance with an anticipated national emission standard, the average of results of all repetitions shall apply.

7.2 Acceptable isokinetic results.

7.2.1 The following range sets the limit on acceptable isokinetic sampling results:

If 90 percent $\leq I \leq$ 110 percent, the results are acceptable; otherwise, reject the test and repeat.

8. References

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